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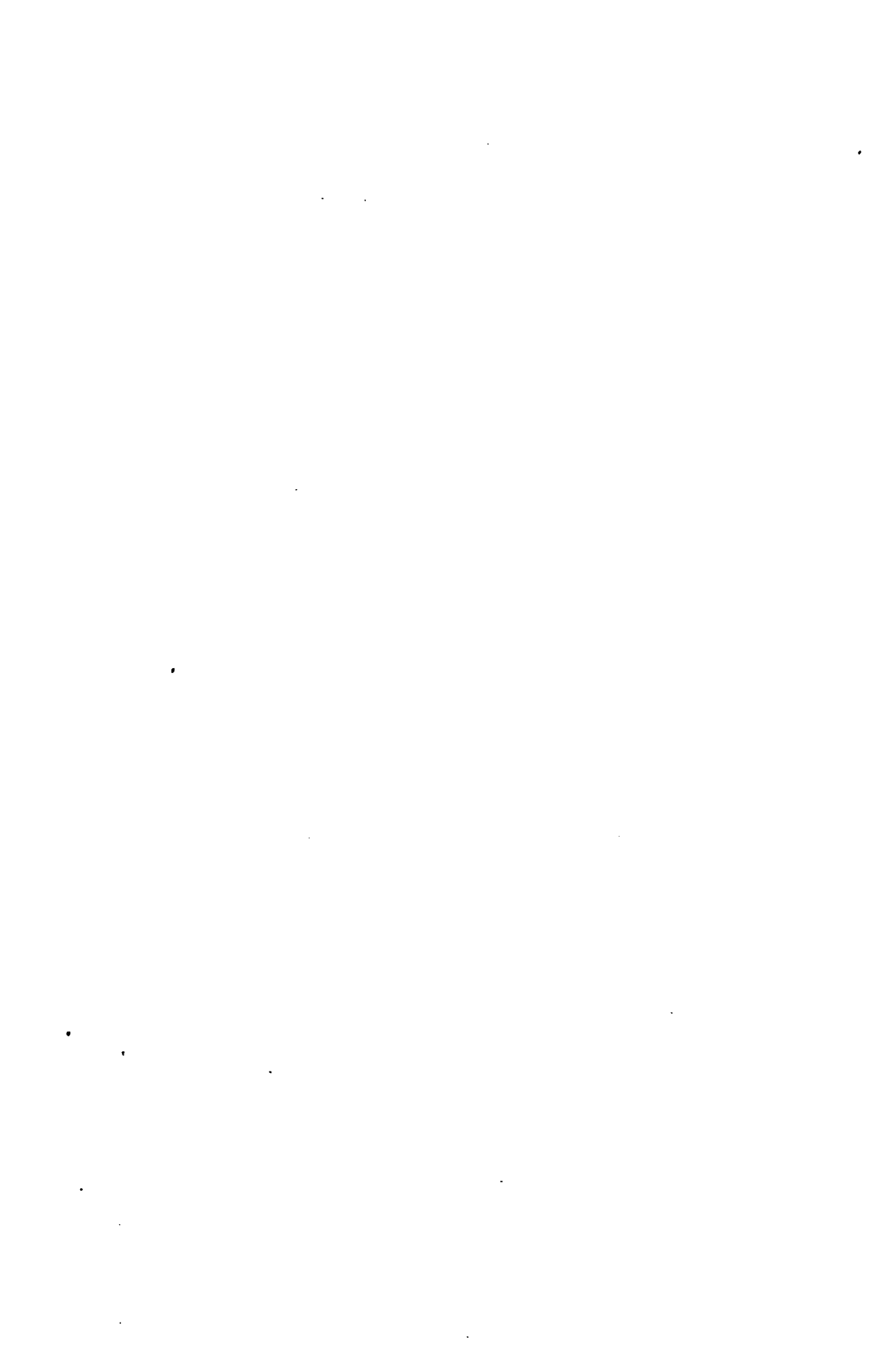
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# COAL-TAR AND AMMONIA



# COAL-TAR AND AMMONIA

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## PREFACE TO THE FIFTH EDITION

THE fourth edition of this treatise appeared in the year 1909. A new issue being called for, the text of the last edition was thoroughly revised, and the vast amount of fresh matter accumulated in the interval was duly added in the proper places. How important these additions have been, is illustrated by the fact that the number of pages, which amounted to 1178 in the fourth edition, has had to be increased to 1718, although very many of the recent communications and patents have been simply quoted, but not extracted. The enormous development of the new processes for the manufacture of ammonia and its salts is the most important factor for this increase.

I may be excused for expressing my hope that the fifth edition will meet with the same favourable reception as its predecessors, and prove equally useful to all those who are interested in the industries of Coal-Tar and Ammonia.

G. LUNGE.

ZÜRICH, 31st March 1916.





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**PART I**

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**COAL-TAR**



# COAL-TAR AND AMMONIA

## CHAPTER I

### INTRODUCTORY

#### *Coal.*

THE first part of this work treats of coal-tar, that pyrogenetic product of the decomposition of coal which is obtained in gas-works and coke-works in large quantities as a valuable by-product. Before we enter upon our proper task, that is, the description of the industry of coal-tar, it seems suitable to consider the raw material, that is, coal as to its formation, its properties, and its occurrence.

*Formation of Coal.*—We shall first quote the utterances of Professor Engler, in his lecture on "Processes of Disintegration in Nature" (*Chem. Zeit.*, 1911, p. 1061), on the processes going on in the formation of coal and petroleum: "Both of these are the residues left in the disintegration of living organic substance, which have not met with the quantity of oxygen required for their complete decomposition by decay. Owing to this lack, the organic substance has not, as in ordinary decay, been altogether resolved by autoxidation into volatile products, but a process of putrefaction has set in, in which the elements of the organic substance have been only partially volatilized by internal re-arrangements of the atoms, so that ultimately, corresponding to the nature of the initial substance (mostly of vegetable origin in the case of coal, and of animal origin in that of petroleum), permanent remainders rich in carbon have been left as coal, or remainders rich in hydrocarbons in the case of bitumen or petroleum. It was therefore a condition for the formation of these products, that the vegetable or animal remainders, previous to their complete decay, were protected



from contact with air, whereby their complete volatilization by oxidation was delayed or entirely stopped, and permanent remainders were left behind. The natural process of decay in these cases led, so to speak, into a blind alley, and those enormous accumulations of incompletely decomposed organic remainders were formed which, after being at rest for many thousands of years, are in recent years, gradually brought to the surface by the hands of men, and now meet with their final destination by being oxidized by combustion into carbon dioxide and water."

"Whilst," Engler continues, "*coal* has been principally formed from the cell-substance and the other vegetable hydrocarbons, there is almost unanimous consent that the substances from which *petroleum* has been formed are the liquid and solid waxes of animal and vegetable beings, originating most likely both from the macro and the micro fauna and flora. . . . In coal the solar energy of long past thousands of years has been stored up, and by its combustion it is the principal source of energy of our industry, which in recent times has taken such a powerful development. Similarly to coal, petroleum is also a product of decomposition, brought about by solar energy. The flame of the petroleum lamp contains the light and heat radiated upon earth thousands and millions of years ago."

It has been established by geologists and palæontologists as an undoubted fact that in the *formation* of the coal-deposits water has played a most important part.<sup>1</sup> Coal has been recognised as the decomposition product of a former vegetable and animal world, the former being greatly prevailing. How far the vegetable world may have consisted of marine plants (*fucus*), or also of terrestrial plants (bog plants, sunken forests), has not yet been securely established. Some coal-beds are undoubtedly of marine origin, but others, the inland beds, owe their formation to local depressions on the continents. The marine beds mostly occupy long stretches on former sea-coasts, where the elements of formation are much the same all over; they are probably formed by marine plants, carried away when dead by naval currents and deposited in certain places. The inland beds, such as the Saar coal-bed, are much less widely extended and much less regular; they are possibly formed by

<sup>1</sup> Cf. Potonié, *Die Entstehung der Steinkohle*, Berlin, 1910.

the floating action of rivers, or by the formation of bogs, owing to the changes of level of the soil. Probably both these factors have contributed to the formation of coal, and this may be an explanation of the differences of properties of different coal-beds.

Evidently the decaying vegetable matter was gradually covered by layers of mud, which later on solidified and turned into the various descriptions of rock (carboniferous sandstone, carboniferous limestone, carboniferous slate) in which the coal is deposited. This is proved by the whole situation of the carboniferous formations as well as by the enclosures of vegetable petrifacts and remainders of terrestrial animals which in all cases occur in coal. But the vegetable remainders of which the coal itself consists were formed during immense spaces of time in the subsequent geological epoch under the influence of pressing heat and internal chemical rearrangements and decompositions into that substance which we now call "coal." It cannot be even approximately estimated how many generations of plants were required for producing the enormous treasures of coal existing in our planet, forming beds up to 250 ft. deep. To be sure, we must remember that during that far-removed geological epoch the high percentage of carbon dioxide in the air, together with the tropical climate, were bound to produce a vegetation entirely differing from that of our own days.

We cannot stop to discuss in this place the various theories enounced on the formation of coal, in respect of their likelihood to represent the truth. But we must oppose a view which up to this day is found in certain scientific treatises, and which evidently starts from incorrect suppositions, since it must produce entirely erroneous views as to the nature of coal. It has been supposed (*e.g.* by Schultz, *Chemie des Steinkohlenteers*, 1882, p. 21) that coal has been formed from the cellulose of terrestrial plants by the separation of *free carbon*, as well as of water, wherein the resins and oils which partially resisted the decay, under the pressure of the superincumbent masses of rock, cemented the carbon particles into a stony mass. The incorrectness of this view is from the outset proved by the fact, to be mentioned later on, that coal in reality does not contain any "free carbon." Moreover, the researches of Hoppe-Seyler (*Berl. Ber.*, xvi., p. 122) and Tappeiner (*ibid.* pp. 1734 and 1740)

have proved that the decay of cellulose takes place under the influence of a ferment found in every bog, forest, and field, not in the just-mentioned way, but already at 20°, the principal products being carbon dioxide and methane, with a secondary formation of hydrogen, sulphuretted hydrogen, and aldehyde. There is no scientific reason for assuming that during the coal period that process was going on in a different manner from that observed at the present time; on the contrary, we may assume that at that period it was going on in an immensely more gigantic way than at the present time.

It cannot be questioned that the various constituents of those coal-forming primeval plants, as cellulose, oils, resins, organic acids, albuminous substances, etc., act in very different manners in the process of decay; but the formation of notable quantities of free carbon is practically excluded. Undoubtedly, the assumption of its formation has in the first line been based upon the black colour of coal; secondly, to the fact that in the gasification of coal a carbon-like residue, coke, is formed. But it has been proved that coke itself must not be considered as (impure) carbon, but is most likely a highly complicated compound of hydrocarbons. Muck (*Steinkohlenchemie*, 1891, p. 1) justly points out that otherwise the pre-existence of free carbon would have to be assumed also in starch, sugar, and other substances which on heating leave a carbonaceous residue. The same line is taken by Guignet (*Comptes rend.*, vol. lxxxviii, p. 590), Frémy (*ibid.*, p. 1048), Baltzer (see below), and Friswell (*Chem. Zeit.*, 1892, p. 904).

#### *Properties and Composition of Coal.*

Coal is a non-crystalline, dense, slaty or fibrous substance, of dark brown up to pitch-black colour, which has frequently a parallelo-epipedic structure, and under the microscope shows vegetable texture. Its specific gravity is from 1.2 to 1.3, and its elementary composition ranges from 80 to 95 per cent. carbon, 2.5 to 6.5 per cent. hydrogen, 2.5 to 20 per cent. oxygen and 1.0 to 2.0 per cent. nitrogen. Experience has shown that the percentage composition of coal affords no possibility of classifying it for technical purposes. This is much better attained by its behaviour at higher temperatures; but here as well there are fluctuations according to the origin of the

various specimens of coal. This subject is treated in detail by Muck in his above-quoted *Steinkohlenchemie*. For our purposes it will suffice to quote the classification of Gruner and that of Herwegen.

Gruner (*Annales des Mines*, 1873, iv., p. 169) gives the following table:—

Classes of coal.	Composition, per cent.			Yield in distillation, per cent.		
	C.	H.	O.	Gas.	Ammoniacal liquor.	Tar.
1. Sand-coal . . .	75 to 80	5.5 to 4.5	19.5 to 15	20 to 30	12 to 5	18 to 15
2. Gas-coal . . .	80 " 85	5.8 " 5.0	14.2 " 10	20 " 17	5 " 3	15 " 12
3. Blacksmith's coal	84 " 89	5.0 " 5.5	11.5 " 5.5	16 " 15	3 " 1	13 " 10
4. Coking-coal . .	88 " 91	6.5 " 5.5	6.5 " 5.5	15 " 12	1 " 1	10 " 5
5. Anthracites (dry coal) . . .	90 " 93	5.5 " 3.0	5.5 " 3.0	12 " 8	1 " 0	5 " 2

For the manufacture of coke, illuminating gas and tar (which alone are of interest to us in this treatise), according to that classification, principally Nos. 1, 2, and 4, are of importance. Sand-coal and gas-coal furnish the best material for the manufacture of illuminating gas, the former in respect of quantity, the latter in respect of quality. The short-flamed No. 4 is, especially after washing and levigating, the best material for the manufacture of coke; these descriptions, therefore, are the proper starting material for coal-tar.

Herwegen (*Kokereitechnik*, 1911) gives the following table:—

Designation.	Composition.			Yield of calories.	Pit moisture.	Yield of coke.	Quality of coke.
	C.	H.	O.				
	P. cent.	P. cent.	P. cent.	Per ton.	P. cent.	P. cent.	
Flaming-coal . . {	80	5	15	7600	4	60	sintered
	82	5	13	7800	3	63	fluxed
Gas-coal . . . {	84	5	11	8000	2	65	"
Coking-coal (bitu- {	86	5	9	8300	2	70	"
minous coal) . . {	88	5	7	8500	1	75	"
Dry coal (non-bitu- {	90	5	5	8800	1	78	"
minous) . . . {	92	4	4	8700	1	80	sintered
	94	3	3	8500	0.5	90	pulverulent
Anthracite . . . {	96	2	2	8400	0.5	95	"
	98	1	1	8200	0.5	98	"

As pointed out above, there is now no doubt on the fact that *coal does not contain any free carbon at all*. Especially Friswell (*loc. cit.*) has shown that the black residue which remains after coal powder has been boiled for six hours with nitric acid of about 49 per cent., and which looks like unchanged coal, has nothing in common with coal. Unlike this, it is almost completely soluble in a dilute solution of sodium hydrate, and from this solution acids precipitate brown flakes, soluble in an excess of water, which after drying behave like a nitro-compound. When distilling this substance with addition of zinc dust hydrogen and cyanogen are given off, and the distillate contains ammonia, with traces of pyridine and other bases.

Most probably coal must not be looked at as a simple chemical compound, but as a mixture of various, most likely very different hydrocarbons of high molecular weight. Basing on this point of view, Baltzer (*Vierteljahrsschr. d. Züricher Naturf. Ges.*, 1873; Muck, *Steinkohlenchemie*) has enounced the following views as to the constitution of coal :—

- 1st. Coals are mixtures of complicated carbon compounds.
- 2nd. These compounds form a genetic, and most probably homologous series.
- 3rd. The carbon skeleton of these compounds is very complicated. The only analogy to it is presented by the aromatic series of organic compounds.

Considering the elementary composition of coal and its large contents of carbon, it seems indicated to look for the cause of its formation and constitution in this: that its principal constituents belong to the aromatic series, and this assumption is all the more justified, as in the destructive distillation of coal the whole series of benzene compounds is formed, which certainly is no proof of the pre-existence of the single members of that series. Anyhow, it is in this respect interesting to learn that Watson Smith and Chorley (*J. Soc. Chem. Ind.*, vol. xii., p. 220) have succeeded in extracting Japanese coal with benzene to obtain somewhat considerable quantities of a bitumen containing aromatic hydrocarbons, phenols, and members of the pyridine and quinoline series, although but in small quantities. We must also notice the results obtained by Guignet (*Comptes rend.*, vol. lxxxviii., p. 590) by the action of nitric acid on coal. He

obtained large quantities of trinitro-resorcine, together with oxalic acid. When fusing it with caustic soda, there were formed, together with humus-like substances, ammonia and aniline.

We also refer to the well-known occurrence of the ammonium compound of mellithic acid,  $C_6(COOH)_6$ , as "honey-stone" in the coal of the quadersandstein and the carbonic formations of the Tula Government, and that of fichtelite in some peat and lignite deposits, which mineral is probably a perhydride of retene (Bamberger and Strasser, *Berl. Ber.*, 1889, p. 3361). Kraus (*Ann. Chem. Pharm.*, vol. xxviii, p. 345) has found retene also in the scheererite of the lignite deposit at Uznach (Switzerland).

Still it must be admitted that these isolated discoveries do not admit of drawing a general conclusion on the chemical nature of coal; Guignet himself ascribes the occurrence of trinitro-resorcine in the treatment of coal with nitric acid to the resinous substances contained in it. Up to the present it is not feasible to propose special structure formulæ for coals of different composition, as some have tried.

Undoubtedly the *resinous* and *wax-like substances* are of special importance for the formation of gases from coal. Muck, in his *Steinkohlenchemie*, p. 45, enumerates a series of compounds of this kind, observed in coal, whose composition and properties are sometimes stated in rather different ways, and which, therefore, cannot be looked at as sharply distinguishable chemical individuals. According to him, Dondorf has observed in Westphalian coal a substance occurring in thin leaves, of black colour, with reddish-brown iridescence, about 0.3 per cent. of which can be extracted from the coal by means of carbon disulphide or ether. It contains 87.22 per cent. C., 0.20 H, 2.29 O, 1.29 S. Its ethereal solution shows strong fluorescence, and it burns with a bright, sooty flame and an incense-like smell. Its occurrence in coal proves that sulphur occurs in coal not merely as a mineral impurity, but also in organic chemical combination. Reinsch (*J. prakt. Chem.*, 1880) seems to have obtained a similar substance. Siepmann (*Stahl u. Eisen*, 1910, p. 1236) has extracted several resinous substances from coal by means of ether, alcohol, and chloroform. Piçtet and Ramseyer (*Berl. Ber.*, 1911, p. 2786) extracted from

300 kilograms of coal by means of boiling benzene, 244 grams of an oil which, after washing with alkali and acid, was separated by repeated fractional distillations into several fractions, none of which contained nitrogen or sulphur, which quickly absorbed oxygen and were turned into resinous matter. All of them showed the composition,  $C_{13}H_{18}$ . They proved that the higher fractions were formed by polymerization from the fraction boiling at  $270^{\circ}$ , which was identified as *hexahydrofluorene*, and which can be also obtained from the coal itself by destructive distillation *in vacuo* at  $450^{\circ}$ . They believe themselves entitled to the conclusion that coal is essentially formed by the polymerization of originally liquid substances.

Rau (*Stahl u. Eisen*, 1910, p. 1236) states that up to that time the extraction of coal by benzene, chloroform, phenol, or other solvents yields at most 4 per cent. of soluble substances. Even at a temperature of  $200^{\circ}$  and a pressure of 14 atmospheres he could not extract from Westphalian "Fettkohle" by benzene more than from 1 to  $1\frac{1}{2}$  per cent. of soluble matter.

Bedson (*J. Gasbeleucht.*, 1908, p. 627) made the important discovery that *pyridine* dissolves from 27 to 35 per cent. from gas-coal (yielding 64 to 66 per cent. of coke). Dennstedt, Hassler, and Bünz (*Z. angew. Chem.*, 1908, p. 1825) obtained from German and English coals, yielding 62 per cent. coke, 18 per cent. pyridine extract; much less, of course, from anthracite-like coals, down to 0.6 per cent. in the case of coal yielding 87 per cent. coke. Wornast (*Stahl u. Eisen*, 1910, p. 1236) obtained 12 per cent. pyridine extract from Lorraine gas-coal yielding 50 per cent. coke, and 29 per cent. extract from Westphalian coal yielding 62 per cent. coke. Rau (*Stahl u. Eisen*, 1910, p. 1236) considers it as a fact that pyridine does not act as a physical but as a chemical solvent; there is nothing definite known as to the nature of the dissolved substance.

Putting all results together, we may say that pyridine extracts less from bituminous matter and from recently formed coal than from gas-coal, the maximum being at coal yielding 65 per cent. coke. Above that the extract is less down to zero in the case of anthracite. Rau considers that, if chemists pay as much attention to coal as they have done to coal-tar, very considerable results for practical application may be expected.

Stahlschmidt (*Z. angew. Chem.*, 1899, p. 790) treated

finely powdered Eschweiler coal with liquid *bromine*, washed the remaining mass with alcohol, and dried the residue at 100° to 110°. He states the composition of the substance before and after this treatment as follows:—

	Before the treatment with bromine.	After the treatment with bromine.
	Per cent.	Per cent.
Carbon . . . .	87.50	47.28
Hydrogen . . . .	4.96	2.61
Bromine . . . .	...	45.50
Nitrogen and oxygen . .	4.13	3.88
Ashes . . . .	2.28	0.73
Sulphur . . . .	1.13	...

The mass remaining after the treatment with bromine yielded on boiling with sodium carbonate solution, 0.7, with ammonia, 7.3, and with caustic potash solution, 42 per cent. bromine. When heating it in a current of carbon dioxide the decomposition, with evolution of bromine, commenced at 200°; at 360° from 13 to 21 per cent. bromine was evolved as HBr, according to the time of heating; on heating over the Bunsen burner all the bromine was driven out.

*Gases contained in Coal.*—Such gases, contained in the pin-cracks of coal, frequently escape under high pressure as “blowers,” and are a great trouble in coal-mining. They have been examined by numerous chemists (Bischöf, Bunsen, Keller, E. von Meyer, Thomas, Schondorff, etc.), and have been recognized as mixtures of ethane, methane, ethylene, butylene, and other members of the series  $C_nH_{2m}$ , carbon monoxide, carbon dioxide, nitrogen, and oxygen. Very likely they have taken their origin in recent times, the coal being still subject at the present time to a further slow carbonization; but the nitrogen and oxygen of the “blowers” are probably simply due to atmospheric air.

*Occurrence of Coal in Nature.*—We speak here only of coal in the proper sense (pit-coal), not of browncoal (lignite), since “coal-tar” in the ordinary meaning is only derived from the former. Coal is, of course, principally found in the “Coal-Measures,” but sometimes also in the Lower New Red Sandstone (Saar), in the Lias (Banate), and in the Wealden.



It is, therefore, the product of processes going back to the older palæozoic formation, which, according to a calculation by Grossmann, dates to about 2,260,000 years before the present time.

*The production of the principal countries during recent years, according to various sources, has been as follows. The figures mean metrical kilo-tons, 1 of which is=984.2 English tons =1102.3 American tons (of 2000 lbs.).*

Countries.	Year.						
	1872.	1882.	1895.	1900.	1906.	1909.	1910.
<i>Europe—</i>							
Belgium . . . .	15,659	...	20,451	23,463	21,775	23,561	23,927
Germany . . . .	42,324	...	79,169	109,290	121,290	217,322	221,986
France . . . . .	15,900	...	27,583	32,722	35,218	37,972	38,570
Great Britain . .	125,473	...	192,705	228,795	239,918	263,775	264,505
Italy . . . . .	...	...	...	...	...	395	400
Austria-Hungary .	10,443	...	10,791	12,440	13,673	39,843	39,214
Russia . . . . .	1,097	...	9,099	16,157	18,688	24,083	24,572
Sweden . . . . .	...	...	...	...	...	250	211
Spain . . . . .	...	...	...	...	...	3,520	3,550
<i>America—</i>							
Canada . . . . .	...	...	...	...	...	9,447	13,011
Mexico . . . . .	...	...	...	...	...	919	2,451
United States . .	41,491	...	175,193	244,653	386,272	402,982	441,617
<i>Africa—</i>							
Transvaal, Natal, and Cape Colony . . .	...	...	...	...	...	4,940	5,500
<i>Asia—</i>							
China . . . . .	...	...	...	...	...	12,840	14,591
Japan . . . . .	...	...	...	...	...	14,020	14,794
India . . . . .	...	...	...	...	...	11,870	12,092
<i>Australia . . . .</i>	942	...	4,360	6,847	7,617	...	...
New South Wales .	...	...	...	...	...	8,132	8,394
New Zealand . . .	...	...	...	...	...	1,942	2,233
Other parts of Australia	...	...	...	...	...	1,184	1,711
<i>All other Countries . .</i>	7,943	...	16,447	25,271	39,248	5,000	7,000
Production of the whole world . . . . .	256,276	319,064	505,800	699,278	853,688	1,083,997	1,140,241

*The entire stock of Coals in the Earth is estimated by Engler (Chem. Zeit., 1911, p. 1062) for the year 1908 at about 700,000 million tons, of which Germany possesses 416,000, Great Britain 193,000, Belgium 20,000, France 19,000, Austria-Hungary 17,000, Russia 40,000. The stock of coal in the soil of the United States is estimated at about 680,000 tons; that of the remaining parts of the world, at least at the same figure; so*

that the stock of coal in the whole world would be about 3,000,000 million tons. At the present rate of coal-mining that stock would last in Germany for another 3000 years, in Great Britain for 700 years, in the remainder of Europe for 900 years, and in the United States for 1700 years.

Of course only part of the coal mined comes into question for the production of tar. According to an estimate of Rau, in *Stahl u. Eisen*, 1910, p. 1296, the percentage of coal worked, with production of tar, in the year 1909 was:—

	Germany.	Belgium.	Great Britain.	United States.
	Per cent.	Per cent.	Per cent.	Per cent.
In coke-works without the recovery of by-products . . . . .	4	5	10	10
In coke-works recovering the by-products . . . . .	16	11	2	2
In gas-works recovering the gas-works . . . . .	4	4	6	1
Therefore rationally only . . . . .	20	15	8	3

### *Destructive Distillation of Coal.*

The process of destructive distillation of organic substances (that is, of heating them beyond the point of decomposition without access of air) is carried on for several industrial purposes. The principal object may be either the dry residue, or the gases evolved, or else the condensed distillate. The latter nearly always separates into two distinct layers—one of which consists of the water pre-existing in the original substance, or formed from it during destructive distillation, holding in solution a portion of the distillate; the other is formed by the condensed products insoluble in water, appearing in the form of a more or less viscid, dark-coloured oil, in some cases lighter, in others heavier, than the watery distillate, and generally known by the name of *tar*.

According as the original materials differ, the products of their destructive distillation differ also; but the difference is much greater in the condensed distillates than in either the solid residue or the permanent gases. The *solid residue* (charcoal, coke) was formerly considered to consist essentially

of carbon and ashes, but it is in reality a mixture of compounds, containing very much C with but little H and O and sometimes N. The different qualities of wood-charcoal, coke, bone-charcoal, etc., are principally caused by the various descriptions and quantities of mineral matter intimately mixed with the "carbon" remaining behind as the residuum of the organic matter, and varying according to the original substance. Besides, it should not be overlooked that the process of destructive distillation is industrially carried on at very different temperatures, by which both the physical nature and the chemical composition of the carbonaceous residue is greatly modified. Probably this plays at least as important a part as the difference between the original materials. In any case it cannot be denied that the *combustible* portion of all carbonaceous residues, so far as the chemical reactions throw light upon it, does not present any great diversity.

The same may be said of the *permanent gases* formed in destructive distillation, part of which remains dissolved in the products of condensation. Carbon dioxide, carbon monoxide, nitrogen, hydrogen, the lowest members of the paraffin series and of the hydrocarbons containing less hydrogen (ethylene, acetylene) are always found. Sulphuretted hydrogen does not occur in the distillation of wood, but occurs regularly in that of coal and of animal matters. The production of these permanent gases for illuminating purposes is the object of a highly important industry, that of the manufacture of illuminating gas, in which now more than ever *coal* predominates almost to the exclusion of all other raw materials, except for very special purposes.

On the other hand, the *watery distillates* differ very much according to the nature of the raw material. In the case of wood, which contains very little nitrogen, these products are of an acid nature, acetic acid being the most important, next to which come methylic alcohol and acetone. The products originating from fossil vegetable substances behave in this respect similarly to wood, if they have been formed in the present or the more recent geological periods—for instance, peat and browncoal (lignite). The acid reaction of the distillate is frequently quoted as a criterion for distinguishing browncoal from real coal. All the methylic alcohol and most of the acetic acid of commerce

are obtained from this source. Real coal, on the other hand, which always contains a certain amount of nitrogen, invariably furnishes a watery distillate whose reaction is strongly alkaline, owing to the presence of ammonia and, to some extent, of volatile organic bases. The bulk of ammonia and ammonia-salts comes from this source, viz., the *gas liquor*, i.e. the ammoniacal liquor of gas-works, which is obtained not merely by cooling, but also by washing of the gas in the scrubbers.

A similar difference exists in the oily distillates, the *tars*. By "tar" we designate all those products of the destructive distillation of organic substances (whether produced by ourselves or by some natural process in these or in former times), which are not miscible with water. They are oily, more or less viscid, of a dark-brown up to a deep black colour, and a peculiar smell. According to the origin of tars, there are great differences among them, both physically and chemically. We may say, generally, that the tar from peat, browncoal, and bituminous shale consists principally of hydrocarbons of the "fatty" (*aliphatic*) series, wood-tar of phenols and their derivatives, and coal-tar, on the other hand, principally of "aromatic" hydrocarbons. But along with the principal constituents there is always a large number of other compounds present: and matters are still further complicated by the fact that through the action of heat the individual compounds are transformed partly into other compounds of the same series, partly into compounds belonging to other series. Owing to this, tar obtained from the same material differs very much in composition according to the temperature of the destructive distillation—nay, even according to the shape of the retorts, which allows the vapours to remain for a greater or less time in contact with the hot sides of the vessel—matters on which we shall speak in detail further on.

This explains why the tars are extremely complex mixtures. Acids (phenols) and bases can be extracted from them by "serial reactions"; but the great bulk of indifferent hydrocarbons can only be separated from one another by fractional distillation, only a few of them by crystallization or by the formation of sulphonic acids, etc. Of these operations the first is often insufficient for isolating the simple compounds, especially those of high boiling-points, since at the boiling temperature the

compounds are frequently decomposed, a drawback which can certainly be lessened by employing a vacuum, and thus reducing all the boiling-points.

The tar from *browncoal* (lignite), as well as that obtained from *peat* and *bituminous shale* (and formerly also from the Torbane-Hill mineral), is manufactured for its own sake as a principal product, and forms the basis of the West-European industry of mineral oils and paraffin, which has proved its vitality even against the enormous competition of American and Russian petroleum, of ozokerite, and of other products found in nature. The other products of the destructive distillation of similar, more recent, fossil substances possess very little or no value, except in the case of some very dense, coal-like browncoals, which furnish good coke and good gas, but no mineral oil. On the contrary, *coal-tar* up to the present is not manufactured as a principal product, the other products playing an inferior part: it is only an accidental but unavoidable by-product of the destructive distillation of coal for the purpose of manufacturing illuminating gas or coke, just as ammoniacal gas-liquor is. It is imperative to condense these two substances in order to purify the gas; but whilst the coke remaining behind in gas-making was always a by-product of considerable value, which materially influenced the cost price of the gas, tar and ammoniacal liquor were for many years regarded as refuse products which were not merely without value, but caused considerable inconvenience and expense for their removal. But since coal-tar and ammoniacal liquor have become starting-points for a chemical industry of enormous extent, they have also become factors contributing very greatly to the revenue of gas-works; and it can hardly be denied that circumstances might occur in which these two substances would be the principal products of the destructive distillation of coal, so that the gas would only appear as a secondary product. It is of historical interest that the first English patent referring to the destructive distillation of coal (that of John Joachun (*sic*) Becher and Henry Serle, dated August 19, 1681) does not treat of the manufacture of lighting-gas, but of "a new way of makeing pitch, and tarre out of pit coale, never before found out or used by any other."

We shall see further on that recently the production of tar

and ammonia as principal objects of the distillation of coal has been the subject of trials carried out on a large scale.

The *hydrocarbons* which are the principal constituents of coal-tar (as well as of Rangoon naphtha and of crude petroleum) belong to very different classes, and the members of these classes are present in very different proportions. Sometimes the "aromatic" hydrocarbons, *i.e.* derivatives of benzene in the widest sense, are altogether prevailing; these are the tars serving as the starting material for the manufacture of coal-tar colours. Benzene, toluene, xylene, naphthalene, and anthracene are the most important hydrocarbons of this class, and with these always occurs phenol (carbolic acid). But in other tars we find, apart from higher phenols, the members of the paraffin and the olefin series which are classed as "aliphatic" hydrocarbons. Some tars contain compounds isomeric with paraffins and olefins, but being in reality hydrogen addition products of aromatic hydrocarbons; these tars are not fit for the manufacture of colours, but merely for that of fuel oil, lubricating oil, and solid paraffin.

As a rule we find members of both series to a certain extent in all tars; phenols are found in tars of every description. The most valuable tars are those containing most benzene and its homologues. Even a slight admixture of aliphatic hydrocarbons greatly diminishes their value for the manufacture of colouring matters, and a more considerable proportion of aliphatic hydrocarbons may render the tar entirely useless for that purpose. Benzene containing much non-nitrifiable oils, and anthracene containing paraffin, are not accepted by the tar-colour works. Therefore those processes for producing tar, which furnish such mixtures, are of very questionable value, and they cannot compete with gas-tar or coke-oven tar.

It is, therefore, of great importance to inquire under which conditions the formation of aromatic or that of aliphatic hydrocarbons becomes prevalent. We shall see later on that differences of temperature are a very important factor in that respect; but they are not everything. Undoubtedly the physical state as well as the chemical composition of the coal distilled is of great influence. Older fossils yield more aromatic hydrocarbons, younger ones more paraffin-like substances and phenols. But even when treating the same gas-coal or coking-

•

coal, a great difference is found according to the way in which the heat is applied. In order to obtain more of the aromatic hydrocarbons, suitable for the manufacture of artificial colours, it is necessary to cause a stronger heat to act upon a thinner layer of coal. If this is neglected, a gradual distillation is brought about which causes in the inner portions of the coal (which is rather a bad conductor of heat), or in the less strongly heated portions of the retort or oven, the formation of more paraffin-like distillates, owing to the less intense heat. These products are so quickly removed from the reach of the hot retort or oven walls that in the condensed products the paraffins are still prevailing. On the other hand, if the coal is spread out in a thin layer and is exposed to intense heat on all sides, the elements of coal during the decomposition of the coal are at once combined to form the products corresponding to the higher temperatures, viz. benzene derivatives and the less complicated phenols, the destructive distillation in this case not being a gradual but a suddenly acting process.

The paper of E. Mills (*J. Soc. Chem. Ind.*, 1885, p. 325), on the formation of tar from vegetable matter, will be noticed later on.

The following papers also treat of the formation of tar: Spatjew (*Chem. Zeit.*, i., 360); Werner von Bolton (*Z. Elektrochem.*, 1902, p. 166).

The composition of *water-gas tar* is described by Downs and Deane (*J. Ind. Eng. Chem.*, 1914, vi., p. 366).

*Historical Notes on the Application of Coal-tar and the  
Products obtained therefrom.*

Before the latter part of the seventeenth century no notice seems to have been taken of the appearance of tar during the heating of coal—a substance of comparatively small importance at that time. One of the pioneers, if not the real originator, of the industry of coal-tar, the German chemist Johann Joachim Becher, describes his observations in the following words<sup>1</sup>:—

“In Holland they have peat and in England pit-coals [Steinkohlen]; neither of them is very good for burning, be it in rooms or for smelting. But I have found a way, not merely to burn both kinds into good coal [coke] which not any more

<sup>1</sup> “Närrische Weisheit, No. 36,” quoted by G. Schultz, *Chemie des Steinkohlentheers*, 2nd ed., p. 5, and faithfully translated here.

smokes nor stinks, but with their flame to smelt equally well as with wood, so that a foot of such coal makes flames 10 ft. long. That I have demonstrated with pit-coal at the Hague, and here in England at Mr Boyle's, also at Windsor on the large scale. In this connection it is also noteworthy that, equally as the Swedes make their tar from firwood, I have here in England made from pit-coal a sort of tar which is equal to the Swedish in every way and for some operations is even superior to it. I have made proof of it on wood and on ropes, and the proof has been found right, so that even the King has seen a specimen of it, which is a great thing in England and the coal from which the tar has been taken out is better' for use than before." We have seen above (p. 14) that Becher protected his invention by letters-patent.

Later on Clayton (1737-38) made some statements on the nature of the products obtained by destructive distillation; besides coke and tar he found that combustible gases were formed at the same time.

About the middle of the eighteenth century the use of coal became more general, and more especially the manufacture of coke for smelting purposes, in lieu of wood-charcoal, began to be practised on a more extensive scale. It is most remarkable that, in the infancy of coke-making, the recovery of tar in that process was already practised, which has only quite recently again come to the fore. A French metallurgist, de Gensanne, describes a kind of muffle-furnace for coking coal and recovering tar, which was working at Sulzbach, near Saarbrücken, before the year 1768.<sup>1</sup> From the description of the tar or "oil" obtained at Sulzbach (it is said to resemble distilled petroleum, and was used for burning in peasants' and miners' lamps), it must have been much nearer in quality to the blast-furnace and the "Jameson" tar (to be mentioned hereafter) than to gas-tar or to the tar nowadays obtained from closed coke-ovens. Gurlt points out that the "Kohlenphilosoph" Stauf (a visit to whose lonely forest cottage near Saarbrücken,

<sup>1</sup> De Gensanne, *Traite de la fonte des Mines*, Paris, 1770, vol i., ch. 12, quoted by Gurlt, *Die Bereitung der Steinkohlen-Briketts*, 188, p. 22. The place is called "Fischbach" here, but "Sulzbach" occurs in the communications made by Gurlt to Mr Watson Smith, and quoted in the *J. Soc. Chem. Ind.*, 1884, p. 602.



in 1771, is vividly described by Goethe, then a student at Strasburg University) seems to have been the originator of that coking-process; he produced from it "oil," bitumen, lamp-black, and had also collected a cake of sal ammoniac from the "burning hill" near by.

One of the patents of that indefatigable inventor, the Earl of Dundonald (No. 1291, of April 30, 1781), describes an invention for coking coal, entitled, "A method of extracting or making tar, pitch, essential oils, volatile alkali, mineral acids, salts, and cinders from pit-coal." The condensation of the volatile portion is effected by mixing steam with it and then applying cold water. This invention does not, however, seem to have been worked out on a large scale; at any rate it must have soon fallen into disuse.

In any case it is certain that the manufacture of coal-tar was never carried out on any extensive scale until it appeared as a necessary by-product in the manufacture of illuminating-gas from coal, the idea of which seems to have occurred, towards the end of the last century, at the same time to the Frenchman Lebon and the Englishman William Murdoch. The former had already recommended the use of tar for preserving timber; but it was the latter who, along with his celebrated pupil Samuel Clegg, really laid the foundation of the enormous industry of gas-making. The first private gas-works was erected in 1798, at the engineering works of Bolton and Watts; the first public gas-works in London in the year 1813, in Paris 1815, in Berlin 1826.

The tar formed in the manufacture of coal-gas necessarily forced itself upon the notice of the gas-manufacturer, since it could not be thrown away without causing a nuisance. It was probably from the first burnt under the retorts; but the method of doing this without giving very much trouble was not understood then. Alex (quoted in Dumas' *Treatise on Technical Chemistry*, translated by Engelhart, 1830, vol. i., p. 743) reports that at the Glasgow gas-works the tar was utilized for the heating of the gas-retorts, by pouring it over the coke and thus making this more easily combustible. In another place (p. 746) he says: "The tar is but rarely utilized; it is possible to make gas from it by running it into retorts which are filled with moistened coke and heated up to a red heat."

We see from this passage that already in the infancy of the coal-gas manufacture the same ways were tried for getting rid of the tar which up to now have claimed the attention of gas-makers, but more successfully now than at that time.

Some of the coal-tar was, no doubt, also used in those times in lieu of wood-tar, as a cheap paint for wood or metals; but it must have been soon found out that in the crude state it is not well adapted for this purpose, as will be shown later on. It was also quickly perceived that in this respect tar is improved by boiling it down to some extent; and as early as 1815 Accum showed that, if this boiling down is carried out in closed vessels (stills), a volatile oil is obtained which may be employed as a cheap substitute for spirits of turpentine. But this distilling-process does not seem to have been carried out to any great extent; and coal-tar remained, for more than a generation from the first introduction of gas-lighting, a nuisance and hardly anything else.

In Germany the first more extensive employment of gas-tar was that for making roofing-felt (which had already before then been made in Sweden by means of wood-tar), for which purpose it has to be deprived of water and the more volatile constituents. Instead of condensing these, they were at first almost everywhere, and later on in many cases, removed by evaporating the tar in open vessels, thus creating a considerable risk from fire. In Germany, Brönner, of Frankfort, was the first (in 1846) to treat the tar for this purpose in a still, and to condense the more volatile tar-oils, from which he prepared a detergent, long after known by his name, and consisting principally of benzene.

Brönner (according to a communication from him to Dr Köhler) also obtained water-white "creosot," and he sold the heavy oils to railway companies for impregnating sleepers. Since at that time there was absolutely nothing published about this subject, and he had no predecessors in this field, he had to overcome very great difficulties. All the other products were burned for soot.

In Great Britain, where the manufacture of illuminating-gas originated, and where it has always been, and still is, carried on to a very much greater extent than on the Continent, the first more extensive utilisation of coal-tar was made by Dr Anderson

already before 1830, in his chemical factory near Edinburgh. As he told Mr Alex (*loc. cit.*), he employed the ammoniacal liquor of the gas-works for the manufacture of sal ammoniac, whilst the tar was boiled in retorts, whereby naphtha was obtained, which was then purified with sulphuric acid and distilled over again. This naphtha was employed by Mackintosh at Glasgow for dissolving indiarubber, for the purpose of manufacturing waterproof clothing. The pitch remaining behind was used for the manufacture of gas. A more extensive industrial employment for coal-tar was first opened out by the invention of Bethell (1838) for preserving timber, especially railway-sleepers, by impregnation with the heavy oil distilled from gas-tar. From that time dates the introduction of tar-distilling on a large scale. The light oils may have been lost even here in some cases; but more usually they were condensed and employed as "coal-tar naphtha" for burning and for dissolving indiarubber.

The day of the light tar-oils came after A. W. Hofmann (1845) had proved the presence of benzene in them, but especially when Mansfield (whose researches will be mentioned in detail hereafter), in his patent-specification (1847), for the first time accurately described the composition of these oils, along with a process for preparing benzene in a pure state and on a large scale, and with proposals for utilizing the tar-oils of lowest boiling-point for lighting purposes. The industrial preparation of benzene was soon followed by that of nitrobenzene, at that time only employed as a substitute for the essential oil of bitter almonds, and known by the French fancy name "essence de Mirbane." But all these applications produced only a limited demand for the light oils which could be made from the rapidly increasing quantities of gas-tar; so that the latter, except in a few local instances, did not attain any considerable commercial value. But a sudden impetus was given to tar-distilling by the discovery of the *aniline colours* (the first of which was Perkin's mauve, patented in 1856), the material which forms their starting-point, benzol, being exclusively derived from coal-tar.

In the centres of industry, where at the same time most illuminating-gas is made, coal-tar was at once converted from a nuisance into a commercial article in great demand at

good prices. Although only about 1 per cent. of the tar is obtained as benzol, this article at first yielded so much profit that the other products of tar-distilling could be sold at low rates, and new markets could be opened out for them. It is true that, as usual, excessive competition led at one time to a great fall in the price of benzol; and as at the same time the sale of creosote-oil and pitch was very poor, tar-distilling seemed to be hardly a remunerative business. But this condition of things passed away. Even at that time a more rational utilization of the by-products permitted working at a profit; and this, so long as tar was at a reasonable price, was fully secured when, through Graebe and Liebermann's discovery of artificial alizarin, anthracene attained a much higher value than any other product from coal-tar.

*General Observations on the Use of Coal-tar for Industrial Purposes.*

At first, as mentioned *supra*, the tar was nothing but a disagreeable by-product in the manufacture of gas, which had to be removed at some expense. In fact, it was a nuisance which, to some extent, impeded the rapid extension of that form of illumination. During the first period of gas-making the tar was simply run to waste; but this was soon stopped by the nuisance caused in the neighbourhood of the works. The first trustworthy note on the value of gas-tar is found in Dumas' *Treatise of Applied Chemistry* (German edition), 1830, vol. i., p. 762), from which it appears that at the Paris gas-works it fetched 8s. per ton, apart from small quantities sold for medicinal purposes at about 1d. per pound.

In England, as we shall see in Chapter V., already before that time attempts had been made to utilize coal-tar by distillation, employing the volatile portions as burning-naphtha and in the manufacture of waterproof clothing, in lieu of essence of turpentine.

But all this amounted only to a local and inefficient outlet for coal-tar: all the more as the gas-manufacture extended at a much greater rate than the above industries. A great change took place after Perkin's discovery of mauve, in 1856. The new industry of coal-tar dyes required correspondingly large

quantities of raw materials, especially benzol and, later on, anthracene; and this naturally led to a great extension of the distillation of coal-tar. In this respect Great Britain just as naturally took the lead, owing to its flourishing gas-manufacture, and she has been ruling the market in respect of tar-products ever since.

Thus coal-tar had acquired considerable value; and, on the other hand, the enormously increasing manufacture of beetroot-sugar greatly stimulated the demand for sulphate of ammonia, employed as manure, and almost exclusively obtainable from the gas-liquor. About 1884, according to a report of the directors of the South Metropolitan Gas Company, the sale of tar and sulphate of ammonia realized the sum of 9s. 5½d. per ton of coal distilled. Since the price of coal was 11s. 9d. per ton, the value of the by-products of gas-making amounted to 82 per cent. of that of the coal employed.

From a private but trustworthy source, the author can quote the following prices obtained for tar and tar-products about that time:—

Coal-tar in 1883 at gas-works, 55s. ; at tar-works, 61s. to 63s. per ton.

Coal-tar in 1884 at gas-works, 35s. per ton.

Pitch, 33s. to 35s. per ton.

Benzol, 50 to 90 per cent., 3s. to 3s. 1d. per gall. (with cask).

Crude carbolic acid, 1s. 8d. to 1s. 9d. per gall.

Light oil (redistilled), sp. grav. 0·967, 7d. per gall.

Crude naphtha, yielding 50 per cent. at 170° C., 1s. 4d. per gall.

Fluid heavy oil, 2¼d. to 3¼d. per gall. in bulk.

Sulphate of ammonia, good grey, 24 per cent., £14, 10s. in bags (had been as much as £20 a few years previous).

According to other sources, the price of 90-per-cent. benzol in 1883 was 14s. per gall. (no doubt only during a short time).

In 1885, however, the price of coal-tar had fallen to about 12s.; during 1886 (in England) it was about 7s. per ton, and that of 90-per-cent. benzol 1s. 8d. per gall.

In 1887, coal-tar fetched 15s., benzol 90-per-cent. 3s. 6d. per

gall, pitch 13s. 6d. per ton, anthracene 1s. per unit, sulphate of ammonia (grey) £12, 15s. per ton.

The following table, prepared from the market reports in the *Journal of Gas Lighting*, etc., shows the market prices of coal-tar in England during a number of years :—

Year.	Price per ton, in shillings.	Average price, in shillings.	Year.	Price per ton, in shillings.	Average price, in shillings.
1895	from 18 to 20	19	1903	from 21·5 to 26·5	24
1896	„ 18 „ 24	21	1904	„ 22·5 „ 27	24·8
1897	„ 17·5 „ 23·5	20·5	1905	„ 18 „ 22	20
1898	„ 13 „ 17·5	15	1906	„ 18 „ 22	20
1899	„ 14 „ 19·5	16·8	1907	„ 14 „ 18	16
1900	„ 16·5 „ 25·5	21	1908	„ 13·5 „ 17·5	15·5
1901	„ 14 „ 18	16	1909	„ 11·0 „ 14·8	12·9
1902	„ 15 „ 18	16·5			

The cause of the great depreciation of the value of coal-tar during recent years is not quite clear. It is true that the great fall in the price of aniline-colours and alizarin, which took place about the same time, and which was undoubtedly caused by over-production, must have influenced the value of coal-tar. Much stress has also been laid on the fact that during those years the most strenuous efforts had been made to obtain benzol, tar, and ammonia from coke-ovens, blast-furnaces, gas-producers, and so forth. But the quantity of tar, of a quality similar to that of gas-tar, which had been actually obtained in Great Britain up to this time, must have been only a small fraction of that produced at the gas-works; the blast-furnace tar and the Jameson tar cannot at all compete with gas-tar, and the producer-tar can hardly be said to be an article of commerce at the present time.

The state of affairs on the Continent was different, especially in Germany. That country is now in a position to furnish almost the whole of the requirements of coal-tar products for its colour-industry, the largest in the world. Nor has this been changed by the exertions made to develop the recovery of by-products in coke-making in Great Britain, where this system had made comparatively slow progress until the last few years.

Whilst the demand of coal-tar products in the manufacture of aniline-dyes and other colouring-matters has been steadily

increasing, this has not been the case with another very promising outlet for benzol, viz., for carburetting lighting-gas. A check has been given to the latter by the development of the incandescent gas light, and recently also by that of acetylene-light and of electric lighting.

The depreciation of gas-tar, caused by the competition of coke-tar, was also owing to the fact that the percentage of benzol in the former has been gradually decreasing with the increasing introduction of producer-firing at the gas-works. It is also a fact that the coal consumed by the latter does not at present yield so much benzol as in former years—probably because the best quality of coal is now used up by the coke-works, as giving a higher yield of coke.

At the present time, the quantity of tar coming into the market from gas-works and coke-works seems to cover the demand, which tells upon the price.

A further decline is not unlikely to take place later on, for it is a well-known fact that if the supply of a certain commodity continuously, even if but slightly, exceeds the demand, its price is lowered far out of proportion to the amount of surplus, and the opposite takes place if the demand exceeds the supply. But whilst in most other cases the effect of this is, up to a certain extent, counteracted by the storage of large quantities, both of the raw materials and of the products of manufacture, and by fluctuations in the production of both, it is very different in our case. Gas-tar, on the one hand, must be produced quite irrespective of the demand, since it cannot be avoided in gas-making, and, on the other hand, its storage for any length of time is a practical impossibility. Hence a comparatively slight excess of the supply, which cannot be checked in the way usual with most other raw materials, generally soon causes an intolerable glut in the market, and must rapidly force down the price.

This case, however, seems to be excluded here. The recovery of by-products in coke-making requires a very costly plant, and extends only as far as the prices of tar and ammonia keep up at a certain figure. On the other hand, the gas-works are at all times in a position to get rid of any excess of tar by burning it under the retorts. Its value for this purpose greatly exceeds that of coke: in Germany it is estimated that it pays

burning the tar under the retorts when its price has fallen below 17s. per ton, but in England the limit must be placed very much below that figure. Another way of dealing with the tar, viz., converting it into gas, has been frequently attempted, but success in that direction is not yet secured.

The fear entertained some years ago, that the enormous development of electric lighting might greatly reduce the manufacture of gas, and consequently the supply of tar, has not been realized. Quite as much gas is produced as in former times, more especially since it is now so much used for heating and for gas-engines; nor has the introduction of water-gas (which is not incompatible with the production of tar) had as yet any influence in that direction. If the demand for tar (and ammonia) should ever increase beyond the capacity of the present producers, there is still a vast field for the production of more tar; for even in Germany there are still a great many coke-ovens working without recovery of by-products, and in most other countries they are in a small minority against the old system, where no by-products are recovered.

If we further look at the various processes for extracting benzene, etc., from ordinary coal-gas, for converting petroleum-residues and other hitherto almost valueless substances into aromatic compounds by the effect of high temperature, and other similar efforts to be mentioned later on, we shall see that there is not the slightest fear of any scarcity of those indispensable raw materials which are the subject of this treatise.

When surveying the manifold sources, not at all, or at least very imperfectly, utilized up till now, from which tar and ammonia can be obtained by means decidedly within our grasp, it would seem useless to speculate, as has been occasionally done, as to what would be the state of affairs if, by processes to be invented hereafter, all the enormous quantities of coal consumed in our households, for raising steam, and for innumerable other purposes (where a recovery of by-products is not at present thought of) should be made to yield up their tar and ammonia as well. It is easy to get out startling figures, say 5,000,000 tons of coal-tar and 1,000,000 tons of ammonium sulphate for Great Britain alone, but such figures are altogether



illusory. They cannot frighten those who are interested in keeping up the price of those materials at a remunerative rate, nor can they offer a solid prospect of benefiting the consumers of those materials—that is, ultimately, the general public; for if ever practicable means should be invented for burning coal in the above-mentioned cases in such a way that the by-products could be collected (perhaps by means of gas-producers), the interest upon the frightful cost of plant and the inevitable working expenses of collecting the tar and ammonia would probably far more than outstrip any profit that might accrue from their sale, taking into consideration the extremely low price which tar and ammonia would command after the opening out of the more accessible sources of supply from coke-ovens, etc., long before the more remote sources just spoken of could come into play.

In the course of time the following state of affairs has established itself. In England, where by far the largest quantity of gas-tar is produced, where benzene was discovered by Faraday, its industrial preparation by Mansfield, the first aniline colour by Perkin, and where the conditions are the most favourable for the purchase of the necessary chemicals as well as for the sale of the colouring-matters, the manufacture of artificial dyes has only risen to moderate dimensions. The same has been the case in France. On the other hand, in Germany and Switzerland the manufacture of coal-tar colours has been established on an enormous scale, so that the tar produced there formerly could only supply a small portion of the benzol and anthracene required, most of it being imported from England and France, partly in the form of aniline. But the employment of the other coal-tar products, especially dead oil and pitch, in Germany has by no means increased *pari passu* with that of benzol and anthracene; the former, very cheap, articles frequently have to seek markets at such distances that the expense of carriage becomes excessive. Moreover, gas-making in Germany is only partially concentrated at a few large centres of industry; very many small gas-works are scattered all over the country, sometimes not even situated near a railway line, and hardly ever on the bank of a canal or navigable river; so that the collecting of tar for a larger tar-distillery does not pay. Hence, up to a short time ago, in Germany and Switzerland, where the manufacture

of coal-tar dyes has reached its greatest development, it has happened that the tar produced at the gas-works has to be burned under the retorts, a state of things which sometimes has partially, but from other causes mentioned before, arisen in Great Britain as well. In this country tar is largely used for the improvement of high roads and the laying of dust thereon, which since the enormous development of the motor-car industry has become a vital question in that country (as well as in the United States), as is evidenced by the innumerable articles on this subject in the technical literature and in the patent records. In Great Britain during recent years, moreover, the manufacture of "patent fuel" from anthracite coke-dust has been carried out, principally for the requirements of the navy, whilst far greater quantities of tar-pitch are sent abroad for the same purpose, principally to Italy. In Germany this subject has also recently received much attention, mostly on the part of the sanitary and the road-making public bodies.

In Germany the development of the tar-distilling industry is intimately connected with the name of Julius Rütgers, who in 1860 built the first factory of this kind, at Erkner, near Berlin, after having, since 1856, worked the impregnation of timber near Breslau, for which he had at that time to get the heavy tar-oils from England. In 1861 followed his tar-works at Niederau, near Dresden, and then many others in Germany, Austria-Hungary, Denmark, and Russia. During the first fifty years about 90 millions of railway sleepers were impregnated in his factories; every sleeper requiring, according to the official specifications, 80 lbs. of tar-oils. Besides him, his co-operator Dr Kraemer must be called the founder of the scientific and technical development of the German coal-tar industry.

#### *Quantity of Coal-tar produced.*

For the earlier statistics on the quantity of coal-tar produced we must refer to the previous editions of this treatise, and we give here only a few notes on this subject, but the recent statistics will be given at greater extent.

In 1883 it was estimated that the coal-tar then produced at gas-works amounted to—

450,000 tons in Great Britain	
85,000 „ Germany	
75,000 „ France	
50,000 „ Belgium	
15,000 „ Holland	
<u>675,000 tons.</u>	

For 1885, Mr Wilson, of the Beckton tar-works, puts the quantity of coal-tar distilled in the United Kingdom at 643,000 tons.

In 1886 the quantity of coal-tar distilled in Holland was 20,000 or 22,000, in Belgium 30,000 tons.

In the United States, in 1886, according to A. von Schauer, 120,000 tons of tar were produced, of which 60,000 were distilled (this seems to be an excess of the reality), 37,000 tons were used in the manufacture of roofing-paper, and 23,000 tons used in the raw state.

From that time onward the tar produced in other industries than that of gas comes more and more to the front, principally that obtained in by-product coke-ovens and blast-furnaces, about which details will be given in the next chapter.

Dr Bueb, chemist-in-chief of the Dessau Continental Gas Company, supplies the following estimate of the quantity of coal used for the manufacture of gas in Europe during 1898, to which we add the corresponding yield of tar, at the estimate of about 5 per cent. :—

	Coal distilled, tons.	Tar produced, tons.
Great Britain . . .	13,333,000	666,650
Germany . . .	3,333,000	166,650
France . . .	2,700,000	135,000
Austria-Hungary . .	830,000	41,500
Scandinavia . . .	433,000	21,650
Belgium . . .	400,000	20,000
Italy . . .	333,000	16,650
Russia . . .	333,000	16,650
Holland . . .	300,000	15,000
Denmark . . .	270,000	13,500
Switzerland . . .	135,000	6,750
		<u>1,120,000</u>

The diagram Fig. 1 is interesting as showing the development of the production of coal from the year 1840 to

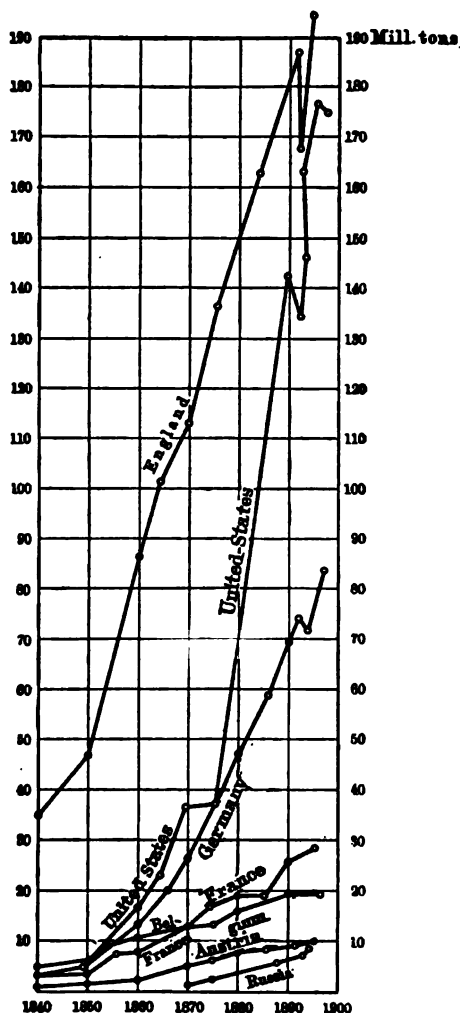


FIG. 1.

1897, which to a considerable extent must keep pace with the production of coal-tar from various sources.

We now give the statistics for later years. Beilby, in a most interesting and suggestive address (*J. Soc. Chem. Ind.*,

1899, p. 647), gives the following statistics concerning the distillation of coal in the United Kingdom at that period :—

	Coal distilled.	Coke produced.	Tar produced.	Sulphate of Ammonia produced.	Gas produced.
	Million tons.	Million tons.	Tons.	Tons.	Million cub. feet.
At Gas-works . .	13	7-8	650,000	130,000	130,000 at 650 { B.T.U. per cub. ft.
„ Blast-furnaces .	2	...	150,000	18,000	360,000 „ 130 „
„ Recovery coke- ovens . .	1½	0-9	62,000	11,000	12,500 „ 600 „
„ Shale-oil works .	...	...	...	37,000	...
If the beehive ovens were entirely re- placed by recovery- ovens, there would be a further produc- tion of . . .	...	...	862,000	196,000	...
	...	9	620,000	110,000	125,000

The 862,000 tons of tar produced were distilled and separated into 474,000 tons pitch and 345,000 tons oils. The increase of these quantities, if not merely all coke were made in recovery-ovens, but also the 130 million tons of coal now burned in the raw state were to be distilled, could not be disposed of in the present way. Beilby discusses the possibilities in that direction, and thinks that the manufacture of briquettes (patent fuel) from the coke would greatly extend and would yield a smokeless fuel. The sulphate of ammonia would more and more take the place of Chilean nitrate of soda. The tar-oils not consumed by other industries would serve as smokeless fuel.

Schniewindt (*Min. Ind.*, x., 152), gives the following estimate of the production of coal-tar in 1901, based on that of ammonium sulphate and gas :—

	Tons.
United Kingdom . . . . .	908,000
Germany . . . . .	590,200
United States (including Water-gas tar) . . . . .	272,400
France . . . . .	190,680
Belgium, Holland, Sweden, Norway, Denmark . . . . .	272,400
Austria, Russia, Spain, and other European countries . . . . .	199,760
All other countries . . . . .	227,000
	<u>2,660,440</u>

Russig, in several papers contributed to the *Chemische Zeitschrift*, estimates the total quantity of coal-tar produced as follows (in tons):—

	In 1900.	In 1901.	In 1902.
United Kingdom, Gas-tar . . . .	692,000	742,000	755,000
„ Blast-furnace tar . . . .	150,000	128,000	156,900
„ Coke-oven tar . . . .	85,000	95,000	122,000
„ Total . . . .	<u>927,000</u>	<u>965,000</u>	<u>1,033,900</u>
Germany, Gas-tar . . . .	180,000	180,000	...
„ Coke-oven tar . . . .	300,000	270,000	...
„ Total . . . .	<u>480,000</u>	<u>450,000</u>	...
United States, Gas-tar . . . .	60,900	(?)	(?)
„ Coke-oven tar . . . .	47,500	50,500	60,100
„ Water-gas tar . . . .	202,100	(?)	(?)
„ Total . . . .	<u>310,500</u>	...	...
France, Gas-tar . . . .	144,000	...	...
„ Coke-oven tar . . . .	35,000	...	...
„ Total . . . .	<u>179,000</u>	180,000	...
Other European states . . . .	355,000	375,000	...
All the world over . . . .	2,270,500	...	...

For the *United Kingdom* the market reports of Bradbury and Hirsch, at Liverpool, state the production of gas-tar:—

1901 . . . .	758,000 tons	1905 . . . .	778,000 tons
1902 . . . .	758,000 „	1906 . . . .	798,000 „
1903 . . . .	764,000 „	1907 . . . .	828,000 „
1904 . . . .	768,000 „	1908 . . . .	828,000 „

According to other estimates, the production of gas-tar in the United Kingdom must have been about 880,000 tons in 1908.

The production of other descriptions of tar in the United Kingdom in 1907 is stated in an official report in the *J. Gas Lighting*, 1909, p. 82, as follows:—

	From Coke-ovens.	From Iron-works.
Tar . . . .	120,000 tons	75,000 tons
Purified tar for paint . . . .	.....	785,000 gallons
Pitch . . . .	5,000 tons	85,000 tons
Heavy tar-oils . . . .	3,364,000 gallons	8,647,000 gallons
Benzol and toluol . . . .	2,358,000 „	721,000 „

The figures for later years are :—

	1900.	1910.
Gas-tar . . . . .	750,000 tons	830,000 tons
Coke-oven tar . . . . .	150,000 „	350,000 „
Blast-furnace tar . . . . .	200,000 „	200,000 „
Total . . . . .	<u>1,100,000 „</u>	<u>1,380,000 „</u>

*United States.*—Russig (*Chem. Zeit.*, iii., 180) estimates the production of coke-oven tar alone in the United States at 75,000 tons for 1903, at 125,000 tons for 1904. Dr Köhler (private information) estimates the production of coke-oven tar in the United States, from 2286 United-Otto ovens and 1320 Semet-Solvay ovens, at 300,000 tons, to which must be added 300,000 tons of tar from gas-works which, however, to a great extent do not furnish ordinary coal-tar, but water-gas tar. Another 1500 ovens were to be built by the U.S. Steel Corporation. Only about 20 or 30 per cent. of the tar produced in the United States finds its way into the distilleries.

According to *Census Bulletin No. 92*, p. 43, the production of tar in the United States was (in short tons of 2000 lbs.):—

In 1900.	In 1906.
69,094 . . . . .	77,643 tons ordinary gas-tar.
222,868 . . . . .	259,934 „ water-gas tar.
52,344 . . . . .	131,117 „ coke-oven tar.
..... . . . .	61,100 „ pitch.
..... . . . .	577,750 gallons purified tar-oils.
..... . . . .	288,817 „ creosote oil.
..... . . . .	17,175 „ other tar-oils.
110,023 . . . . .	127,758 tons gas- and coke-tar distilled.

The total production of coal-tar in 1907 was 466,000 tons.

„ 1908 „ 455,700 „  
 „ 1909 „ 401,120 „

According to I. J. O'Neill (*Progr. Age*, 1911, p. 960) the total production of coal-tar in the United States at that time (1910?) amounted to 100,000,000 gallons. About 56,000,000 gallons were distilled; the remainder was used for roofing-felt, for tarring the streets, and recently also for replacing petroleum in the iron and steel industry; to some extent also as fuel for raising steam. The production of *pitch* was about 200,000 tons, mostly used as soft pitch or “prepared tar.” In the course of 1912, 700 miles of road were to be tarred in the state of New

York, requiring 11,000 to 14,000 gallons "prepared tar" per mile. Of *creosote oil* the United States at present produces only 14,000,000 gallons, whereas in 1909 another 37,600,000 gallons were imported, chiefly from England and Germany. American tar yields on the average 20 to 25 per cent. creosote oil and only 1 per cent. light oils. At present America can only in the crude materials (pitch, creosote, and light oil) compete in its own markets with Germany, but not in purified products, and least of all in the aniline colour industry. The only possibility of development is perhaps in the recovery of benzol as by-product from coking.

From the "Mineral Resources of the United States" for the year 1912 we take the following figures for the production of the United States, for the years 1908 and 1912:—

	1908.		1912.	
	Quantity.	Value, \$1000.	Quantity.	Value, \$1000.
Gas (millions of cubic feet) . . .	53,562	37,228	89,693	36,682
Coke (thousands of short tons) . . .	6,253	21,507	12,491	48,380
Tar (thousands of gallons) . . .	101,262	2,537	134,796	3,802
Sulphate of ammonia (thousands of pounds)	44,093	1,323	99,071	3,741

Hence the production of coal-tar had increased within the five years from 1908 to 1912 by 33 per cent. in quantity and by nearly 50 per cent. in value. The average value of a gallon of tar in 1908 was 2.5 cents; in 1912, 2.8 cents. Coal-tar is in the United States principally used for road-making and for pickling railroad sleepers. The tarring of roads has proved to be very necessary, in consequence of the great development of the motor-car industry; and the pickling of timber, in consequence of the increase of the price of timber. Tar and tar-oils are also employed for the manufacture of roofing-felt and for that of "patent fuel."

Of the tar, produced in 1912, 167,000 tons came from gas-works, and 397,000 tons from coke-ovens.

In *France* the first 210 by-product coke-ovens were started in 1898 and produced 22,000 tons tar. For 1900, Russig estimates the French production of gas-tar = 140,000 tons; of



coke-oven tar = 35,000; altogether, 179,000 tons. For 1901, the total = 180,000 tons. In 1909, from gas-works, 144,800 tons; from coke-ovens, 70,000; altogether, 214,800 tons.

In *Belgium* the total production of tar from all sources was estimated for 1911 = 124,000 tons.

In *Austria* in 1911 there was produced gas-tar 72,000 tons; coke-oven tar, 82,000 tons.

In *Italy* in 1910 the production was 37,000 tons gas-tar, 4207 tons light tar-oil, 5273 tons heavy tar-oil.

For Germany, Haarmann (*Glückauf*, 1906, p. 421) gives in detail the figures for the production of coke-oven tar (see the details on coke-oven tar production in Chapter II.) from 1897 to 1904, in which year it reached 175,863 tons in the Ruhr district, and 276,805 tons for all Germany—against only 18,000 tons in 1887. To this must be added the gas-works tar, estimated by Bunte at 225,000 tons for 1904, thus yielding a grand total of 500,000 tons. For 1906 Köhler estimates the quantity of coal-tar worked up in Germany at 600,000 tons, for 1907 at 675,000 tons from all sources. For 1908 Dr Spilker (private communication) estimates the quantity of tar used in Germany at 900,000 tons, of which 700,000 tons are got westwards of the Elbe.

Special statistics on the production of tar from coke-ovens will be given in Chapter II.

The following statistics were collected by Dr H. Köhler for the last German edition of this treatise, and are to a great extent due to Dr Hönigsberger, of the Deutsche Teerprodukten-Vereinigung at Essen (Ruhr), and to the Verein Deutscher Gas- und Wasserfachmänner.

The German production of gas-tar was, in the year 1907, 318,000 tons; in 1908, 350,000 tons: coke-oven tar in 1907, 534,218 tons; in 1908, 589,500 tons; in 1909, 640,600 tons. The German production of all kinds of tar (except oil-gas and water-gas tar) in 1907, 852,218 tons; in 1908, 939,500 tons; in 1909, about 1,000,000 tons.

The quantity of oil-gas tar is estimated for 1908 at 9000 tons, that of water-gas tar about 3000 tons.

The following figures on the industries of gas-tar, coke-tar, water-gas tar, and oil-gas tar in the years 1908 and 1909 are found in an official report of the German Home Office.

There were at that time in Germany 75 works of that class (including the roofing-felt factories), employing 2997 persons; in 1909, 91 works. The quantities of raw materials worked by them were (in tons):—

A. Tar distilled—		1908.	1909.
(a) Coke-oven tar . . . .		593,522	675,518
(b) Gas-tar . . . . .		207,235	223,856
(c) Water-gas tar . . . .		3,095	1,386
(d) Oil-gas tar . . . . .		8,125	8,167
		<u>811,977</u>	<u>908,927</u>
B. Half-products of Tar Distillation			
<i>worked up—</i>			
(a) Crude benzol . . . . .	16,570		14,307
(b) Light tar-oils . . . . .	1,947		5,082
(c) Heavy tar-oils (creosote and anthracene oils) . . . .	18,814		19,827
(d) Crude naphthalene and crude anthracene . . . . .	6,768		8,454
(e) Crude phenols . . . . .	793		3,735
(f) Crude pyridine . . . . .	7		125
(g) Coal-tar pitch . . . . .	325		

The *annual production* of the German tar-distilleries (exclusive of the benzols and ammonia turned out at the coke-works themselves) was (in tons):—

	1908.	1909.
A. Tar-pitch, including soft pitch . . . . .	402,676	455,221
B. "Prepared tar," Distilled tar . . . . .	83,706	91,520
C. Heavy tar-oils (including carbolic oil, creosote, naphthalene oil) . . . .	248,103	287,854
D. Naphthalene, crude . . . . .	19,713	23,730
Naphthalene, pure . . . . .	16,684	13,497
E. Anthracene, crude and pure, all calculated as pure anthracene . . . .	4,026	3,548
F. Pyridine bases . . . . .	385	336
G. Phenols, cresols, etc.—		
(a) Crystallized carbolic acid . . . . .	1,000	2,211
(b) Cresols (so-called 90, 95, or 100 per cent. carbolic acid) . . . . .	2,081	2,665
(c) Crude phenols for sale . . . . .	581	604
H. Benzol, crude, purified, and pure . . . .	13,229	19,122
I. Toluol, crude, purified, and pure . . . .	2,601	2,791
K. Xylol (Solvent naphtha, heavy benzol, crude and purified) . . . . .	4,717	5,011
L. Other products of tar-distilleries . . . .	4,160	9,008

	1906.	1909.	
M. Concentrated ammoniacal liquor .	118 tons =	24 tons $\text{NH}_3$	11
N. Sulphate of ammonia (24·7 per cent. $\text{NH}_3$ ) . . . . .	1174 „ =	286 „	1,827
O. Liquor ammoniæ, pure . . . . .	935 „ =	206 „	769
P. Sal ammoniac . . . . .	59 „ =	16 „	27

(The items M, N, O, P evidently refer only to the ammonium compounds contained in crude tar, and recovered in working this up.)

Since the German coke-works in 1908 produced 632,378 tons of tar, the above figures show that most of the coke-oven tar had been worked up at German tar-distilleries.

In the course of time the commercial situation of the coal-tar industry has been changed to a great extent. Whereas formerly its principal source of profit was the sale of benzene, naphthalene, anthracene, and other materials for the manufacture of coal-tar colours, nowadays the development of the recovery of benzol in coke-making has nearly driven the tar-works out of the market for this article, and the prices of naphthalene and anthracene have considerably gone down, so that the former by-products of tar-distilling, viz., heavy oils and pitch, now form the principal item in its profit calculations. This will be easily understood from the following figures. In Germany there was produced:—

	In 1900.	In 1909.
Coke-oven tar . . . . .	300,000 tons	640,000 tons
Gas-tar . . . . .	180,000 „	350,000 „
	480,000 „	990,000 „

In the same country the quantity of benzol produced has been:—

	From coke-oven gases.	From coke-oven tar.	From gas-tar.
In 1896 . . . . .	4,000 tons	?	?
„ 1904 . . . . .	34,000 „	4,000 tons	2,000 tons
„ 1908 . . . . .	80,000 „	10,000 „	?

The German production of benzol has been:—

1890.	1896.	1901.	1904.	1908.
4,000	7,000	28,000	40,000	90,000 tons

## CHAPTER II

### PROCESSES FOR OBTAINING COAL-TAR

#### A. *The Production of Coal-tar at the Gas-works.*

FORMERLY nearly the whole of the coal-tar was obtained as a by-product in the manufacture of ordinary coal-gas for illuminating purposes, and formerly, therefore, the denominations "coal-tar" and "gas-tar" were practically identical and were both in constant use. Nowadays the quantity of tar obtained as a by-product in coke-making and from blast-furnaces has enormously increased, and, on the other hand, that due to gas-making has decreased, owing to the extension of carburetted water-gas, etc. Since thus the manufacture of coal-tar from other sources has become practicable, we must call "gas-tar" that particular kind of coal-tar which is obtained in the process of gas-making as an involuntary by-product, to be sharply distinguished from coke-oven tar, blast-furnace tar, water-gas tar, and oil-gas tar.

It is not within the scope of this treatise to give a description of the ordinary contrivances for condensing the tar, which belong entirely to the domain of gas-making. It is sufficient to mention that the constituents of the tar escape from the gas-retorts in the form of vapour, with a little solid free carbon in an extremely finely divided state; they are precipitated in the hydraulic main, in the condensers, scrubbers, etc., in a liquid state, at the same time as the ammoniacal liquor is formed. In one particular instance,<sup>1</sup> of 100 parts of tar altogether obtained, there was found 61.6 in the hydraulic main, 11.8 in the condenser, 26.6 in the scrubbers. The tar formed in the hydraulic main is, of course, poorer in the more volatile products than that formed in the condensers and scrubbers, and is consequently much

<sup>1</sup> Schultz, *Steinkohlentheer*, 2nd ed., i., p. 43.

thicker than the latter; but it is usual to mix all these descriptions of tar in the cistern where they collect, along with the ammoniacal liquor.

The quantity, and to a much greater extent the quality of the tar are influenced by the *nature* of the *raw material* and by the *temperature* at which the decomposition of the coal is carried on. Some coals at low temperatures yield 16 gall. of tar, with 9000 cub. ft. of gas per ton of coal, whilst at high temperatures the same coal yields but 9 gall. of tar, with about 11,000 cub. ft. of gas.<sup>1</sup> If the temperature be comparatively low, mostly such hydrocarbons are formed as belong to the paraffin (methane) series, having the general formula  $C_nH_{2n+2}$ , along with olefines,  $C_nH_{2n}$ . The lower members of these series are liquid, and, furnished in the pure state, are lighting- and lubricating-oils; the higher ones are solid and form commercial paraffin. They are always accompanied by oxygenized derivatives of the benzene series (phenols); but of these the more complicated ones predominate, in some of which methyl occurs in the benzene nucleus, in others replacing the hydrogen or hydroxyl:—*e.g.*, cresol,  $C_6H_4(CH_3)(OH)$ ; guaiacol,  $C_6H_4(OH)(OCH_3)$ ; creosol,  $C_6H_3(CH_3)(OH)(OCH_3)$ , etc. Liquid products prevail; and among the watery ones acetic acid (which is again a compound of the fatty series) is paramount. Of course also permanent gases are always given off, though in comparatively small quantity.

If, on the other hand, the coal has been decomposed at a very high temperature, the molecules are grouped quite differently. Whilst the olefines and members of the acetylene series still occur more or less, the hydrocarbons of the paraffin series disappear almost entirely; and from them are formed on the one hand compounds much richer in carbon, on the other hand more highly hydrogenized bodies. The latter always occur in the gaseous state; hence the gas so produced contains methane or marsh-gas,  $CH_4$ , and free hydrogen as principal constituents, and is very much increased in quantity. The carbon thus set free is partly deposited in the retorts themselves, and then occurs in a very compact graphitoidal form; some of the free carbon occurs in a state of extremely fine division in the tar, and forms a constituent of the pitch or coke remaining behind from tar-

<sup>1</sup> Davis, *J. Soc. Chem. Ind.*, 1886, p. 5.

distilling; another portion contributes to the formation of compounds richer in carbon, belonging to the "aromatic" series, all of which are derived from benzene,  $C_6H_6$ . At the same time the action of heat effects further molecular "condensations," usually with separation of hydrogen, by which process compounds of a higher molecular weight are formed, as naphthalene, anthracene, phenanthrene, chrysene, etc. The never-absent oxygen must also in this case cause the formation of phenols; but here phenol proper, or carbolic acid,  $C_6H_5(OH)$ , predominates, whilst cresol and the other homologues are diminished in quantity, and the dioxybenzenes, as well as their methylated derivatives, disappear altogether.

This is illustrated, for instance, by the statement in Kerl-Stohmann's *Chemie*, 3rd ed., vol. vi., p. 1162, according to which Zwickau glance-coal yielded the following quite different products, according to whether it was put in a cold retort and gradually brought to a red heat (*a*), or distilled quickly from a very hot retort (*b*):—

	<i>a.</i>	<i>b.</i>
Coke . . . . .	60	50
Water . . . . .	10.7	7.7
Tar . . . . .	12	10
Gas and loss . . . . .	17.1	32.1

The tar from *a* consisted of photogen, paraffin oil, lubricating-oil, paraffin, and creosote; that from *b*, of benzene, toluene, naphthalene, anthracene (together with heavy oils corresponding to the paraffin and lubricating-oil), and much creosote.

Börnstein (quoted in Bertelsmann's *Lehrbuch der Leuchtgasindustrie*, 1911, vol. i., p. 39, obtained entirely different results in gas-making from Westphalian coal, if, on the one hand, he carried out the process slowly and at low temperatures (about  $450^\circ$ ), or, on the other hand, quickly and at high temperatures ( $1100^\circ$  to  $1200^\circ$  C.), as proved by the following figures:—

Obtained from 1000 grams coal.	At $450^\circ$ .	At $1100^\circ$ to $1200^\circ$ .
Water . . . . .	43 grams	51 grams
Tar . . . . .	75.3 "	52 "
Gas . . . . .	43.4 litres	40.8 litres
Coke . . . . .	842.8 grams	661 grams

The tar obtained at  $450^\circ$  was brown and oily; it contained solid paraffins and xyleneols; the gas-liquor, besides ammonia,

contained pyridine bases, phenol, and pyrocatechine. But the tar obtained at  $1100^{\circ}$  to  $1200^{\circ}$  was deeply black, viscid, and strongly impregnated with free carbon; it contained much pitch, benzene hydrocarbons, naphthalene, and anthracene and cognate substances, but only traces of aliphatic hydrocarbons.

Similar differences were observed in the composition of the coke, and even more so in that of the gases, as follows:—

	At $450^{\circ}$ .	At $1100^{\circ}$ to $1200^{\circ}$ .
Carbon dioxide . . . .	3.8 per cent.	2.5 per cent.
Heavy hydrocarbons . . .	5.6 „	5.0 „
Carbon monoxide . . . .	3.8 „	9.0 „
Hydrogen . . . . .	17.3 „	47.0 „
Methane . . . . .	57.3 „	34.0 „
Ethane. . . . .	15.2 „	...
Nitrogen . . . . .	...	2.5 „

Behrens<sup>1</sup> found that the tar obtained in the distillation of coal in the ordinary fireclay gas-retorts was much richer in benzene, toluene, naphthalene, etc., than the tar made in Pauwels's coke-ovens from the same kind of coal. The latter is of less specific gravity and contains more liquid (paraffinoid) hydrocarbons, also far more substances soluble in alkalis, but hardly any carbolic acid. We shall further on treat in detail of the differences between tars obtained in various processes of coal-distilling, carried on for other purposes than gas-making.

The same cause explains the difference between the tar of wood-gas works, that of wood-vinegar works, and that of charcoal-heaps (*Meilers*). The former, produced at a very high temperature, is black, thin, smells almost like coal-tar, and contains much real phenol, along with benzene, toluene, naphthalene, etc. The tar obtained at a lower temperature, especially that from the charcoal-heaps, contains mostly cresol and guaiacol in place of phenol, and paraffin instead of naphthalene; it has a lighter brown colour and a much milder smell.

A further difference between distillation at high and at low temperatures is stated to consist in the fact that most of the nitrogen appears in the former case in the shape of aniline and fatty amines (ethylamine, propylamine, amylamine); in the latter case in that of bases of the pyridine series, along with

<sup>1</sup> *Dingl. polyt. J.*, vol. ccviii., p. 362.

picoline, lutidine, viridine, etc. But this requires to be verified by more detailed investigations.

*Differences among the tars from various raw materials.*—Of course it is not possible to obtain the above products in any desired quality from any one of the raw materials here alluded to, merely by altering the temperature of the destructive distillation. It had, for instance, been doubted whether real benzene can be obtained at all by direct distillation from more recent deposits, as peat, browncoal, some sorts of bituminous shales, etc. This matter has been cleared up by Heusler (*Berl. Ber.*, 1892, p. 1665; 1895, p. 448), who proved that the distillate from lignite between 80° and 93° contains 34 per cent. benzene, and that between 100° and 110° 45 per cent. toluene; he also found the higher homologues up to cymene, naphthalene, thiophens, ketones, nitriles, and naphthenes; whilst in Scotch shale-oil he could find only traces of benzene and toluene, and no naphthalene at all. At all events, these materials can in no case serve for a profitable extraction of benzene and the other aromatic hydrocarbons. Wigan cannel coal, if used alone, instead of, as is usual, being mixed with less bituminous coals, yields tars containing so much paraffin that no tar-distiller will take them (Watson Smith). On the other hand, photogen, paraffin oil, etc., cannot be profitably made from coal by distillation at a lower temperature;<sup>1</sup> for cases like that of the Zwickau coal, mentioned above, do not furnish a rule for industrial practice, which has proved that even among brown-coals only certain light, earthy descriptions ("Schweelkohle") are adapted for the manufacture of lighting-oils. But we shall see that it is at least in our power, by *subsequent overheating*, to split up the fatty products (paraffins) from browncoal and petroleum, to a great extent, into gases and aromatic compounds; and to this, no doubt, the illuminating-power of oil-gas and the gas made from petroleum-residues is mainly due.

Our present task lies only with the treatment of real coal. We must remember that at a lower temperature less permanent gases and more methylated derivatives (toluene, xylene, higher

<sup>1</sup> Professor Dittmar, of Glasgow, informs me that about 1875, at Manchester, oils of the formula  $C_nH_{2n+2}$  were made by the distillation of coal at a low temperature. But no doubt this was cannel coal, which in that respect occupies a place between real coal and more recent fossils.



phenols), at a higher temperature more gases, along with benzene, naphthalene, anthracene, and far more free carbon, are formed. At very high temperatures the tendency to complete dissociation becomes far more pronounced; the products approach more and more to free carbon on the one hand, and free hydrogen on the other; but this end itself is never actually reached at the temperature attainable by us. Most gas-engineers try above everything to get as much gas as possible out of the coal, and therefore distil at the highest possible temperature. Up to a certain point this is quite rational, and is even unavoidable from the nature of the material now universally employed for gas-retorts, viz., fireclay. This point seems to be reached when the fatty compounds are split up as far as possible before any considerable separation of free carbon has taken place. Beyond this point more gas will be got, but its lighting-power will be less; the tar will at first contain rather less anthracene, and more naphthalene, which has much less value, also more phenanthrene, pyrene, chrysene, diphenyl, etc., which are at present valueless; so that its value on the whole will be less. There is also a reduced quantity of tar, if the temperature in the retorts is raised higher. The separation of free carbon in the retorts and the tar is also largely increased. In England the usual temperature of working seems now to be about  $1100^{\circ}\text{C}$ . ( $2000^{\circ}\text{F}$ ).

For the temperature of working at some German gas-works Schaefer (*Einrichtung und Betrieb eines Gaswerkes*, 1910, p. 979) gives the following figures:—

(a) *Horizontal Retorts* (Mannheim).

Retorts.			Furnace.
Left side.	Centre.	Right side.	
1011°	1078° 1032°	1007°	1309°

(b) *Slanting Retorts.*

Retorts.			Furnace.	
Left side.	Centre.	Right side.	Centre.	Sides.
1056°	1070° 1054°	1037°	1256°	1184°

(c) *Coke-furnace* (Imp. Cont. Gas. Assoc., Berlin).

Above the retorts	.	.	.	1232 to 1464°
Closely above the producer	.	.	.	1264 „ 1464°
Fifth flue	.	.	.	1002 „ 1126°
Last but one flue	.	.	.	918 „ 992°

Properly speaking, it should be experimentally ascertained (and that for every class of gas-coal specially) at what temperature the maximum of lighting-power is obtained, even if concentrated in a smaller volume of gas, and also at what temperature we can get a maximum yield of benzene, toluene, phenol, and anthracene in the tar. Probably the two maxima will not coincide; and it will then be a matter of business calculation whether the one or the other is to be worked for. It is evident that the market prices of the tar-products will influence this consideration largely, and that any diminution in the price of gas will turn the scale in favour of richer tar.

Experiments in this direction have been made at the Testing Station of the German Society of gas- and water-engineers. They show for Saxon gas-wal, carbonized at various temperatures (stated in the first column), the heating-values and the lighting-power (per 100 kg. at 0° and 760 mm.).

Furnace temperature.	Heating-value.		Lighting-power of the gas.
	Upper.	Lower.	
1050° . .	6113	5503	14.56
1165° . .	5830	5213	12.84
1180° . .	5815	5220	...
1200° . .	5675	5023	...
1210° . .	5660	5101	11.65
1250° . .	5623	5031	9.82

This proves that with the rise of temperature on carbonization the heating-values are increased, but the lighting-power of the gas obtained is lowered to such an extent that the greater yield of gas cannot make up for the loss.

It is quite certain that the composition of coal-tar was very different from what it is now at the time when coal used to be distilled in cast-iron retorts, necessarily at a considerably lower temperature than the above-mentioned 1100° C., which applies to fireclay retorts. The higher temperature existing in the latter is certainly to some extent counterbalanced by the action of the exhauster, which causes the gases to remain a shorter time in contact with the heated sides of the retort. The exhauster also makes the tar thicker, by carrying away a good deal of coal-dust from the retort in a mechanical way.

L. T. Wright (*J. Soc. Chem. Ind.*, 1886, p. 559) states that as the distillation-temperature is increased the tar decreases slightly in quantity, but increases in specific gravity. Above a certain temperature, which differs for each kind of coal, the trouble caused by thick tar stopping up pipes, etc., prevents the gas-making process from being carried on. In the average of gas-works the distillation-temperature is as high as can be conveniently attained with the present form of gas-making plant, so that there is practically no margin for any reduction in the output of tar by the employment of higher temperatures.

The following table serves to illustrate the variations in the volume and weight of tar (and gas) yielded by coals distilled at

Description of Coal.	Temperature of distillation.	Cubic feet of gas per ton.	Gallons of tar per ton.	Spec. grav. of tar.	Pounds of tar per ton.	Weight per cent. on coal.
Derbyshire Black Shale, No. 1 .	very high	11,128	10.63	1.210	128.62	5.74
" " "	normal	10,400	...	1.185	...	...
" " "	very low	7,856	11.50	1.145	131.67	5.88
Derbyshire Black " Shale, No. 2 .	very high	11,190	12.01	1.207	144.96	6.47
" " "	normal	10,400	...	1.185	...	...
" " "	very low	7,562	14.38	1.136	163.35	7.29
Notts "Top Hard" Cannel .	normal	9,852	21.32	1.147	244.54	10.92
" " "	very low	7,125	23.81	1.116	265.72	11.86

widely different temperatures. The experiments were conducted in clay retorts with the ordinary form of gas-plant. The expression "normal temperature" means the highest practically and continuously possible in a modern gas-works; by "very high temperature" is meant one only practicable by careful nursing and for a short period.

Later on (*J. Gas Lighting*, 1888, p. 169) the same author made the following statements:—

Derbyshire Silkstone coal, of the following composition: C=75.71; H=6.27; S=1.72; N=1.72; O=11.59; ashes=2.99, yielded, on carbonization, for each 100 kg. of tar:—

At about 800° C.: 64.75 kg. coke and 6.43 litres tar, spec. grav. 1.0, with about 15 per cent. free carbon;

At about 1100° C.: 64.16 kg. coke and 5.37 litres tar, spec. grav. 1.207, with about 25 or 30 per cent. free carbon.

The same writer (*J. Soc. Chem. Ind.*, 1888, p. 59) examined the composition of tar, yielded by the same kind of coal (C=81.92; H=5.39; N=1.28; S=1.97; O=6.88; ashes=2.56) at different carbonizing temperatures, between 600° and 800° C.:—

	I.	II.	III.	IV.	V.
Cubic feet of gas yielded per ton of coal	6600	7200	8900	10,162	11,700
Specific gravity of tar	1.086	1.102	1.140	1.154	1.206
Composition of tar per cent. weight:—					
Ammoniacal liquor	1.20	1.03	1.04	1.05	0.383
Crude naphtha	9.17	9.65	3.73	3.45	0.995
Light oil	10.50	7.46	4.47	2.59	0.567
Creosote oil	26.45	25.83	27.29	27.33	19.440
Anthracene oil	20.32	15.57	18.13	13.77	12.280
Pitch	28.89	36.80	41.80	47.67	64.080

We see that with the rise of temperature the yield of naphtha and light oil sinks from 20 per cent. to 1.5 per cent., and that of pitch rises from 29 per cent. to 64 per cent. The yield of benzol from the crude naphtha (boiling up to 100° C.) fell with the rise of temperature, whilst naphthalene increased. The crude naphtha of the light tars contained up to 5.0 volume per cent. of liquid paraffins, that of the heaviest tar only 1.0 vol. per cent. Anthracene seems to be formed mostly at medium temperatures; the maximum, 0.370 per cent., was found in tar of spec. grav. 1.140, whilst the lighter and heavier tars contained less of it.

This agrees with Kraemer's experience (*J. Gasbeleucht.*, 1887, p. 849), according to which tar distillers prefer the tar from smaller gas-works, whose retorts are fired with coke, to that from large gas-works, provided with gas-producer fires and working at higher temperatures.

Watson Smith (*J. Soc. Chem. Ind.*, 1889, p. 950) relates similar observations. With the rise of temperature he found in the tar more naphthalene and anthracene. The carbolic acid appeared not merely in the middle oils, but also in the heavy oils, from which it can be recovered by Lowe's B. P., 3005, of 1872.

Hilgenstock (*J. Gasbeleucht.*, 1902, 617) attributes the

notorious difference between gas-tar and coke-oven tar with respect of their contents of free carbon and other products of pyrogenetic decomposition to the fact that in coke-ovens the escaping vapours do not attain temperatures above  $600^{\circ}\text{C}$ ., and that they are moreover protected against decomposition by the dilution of the heavy vapours, slowly given off from the interior of the coal block, with the fire-resisting gases escaping at the same time from the outer zone of the block. On the other hand, in the case of gas-retorts, the heavy vapours escape at once undiluted by the fire-resisting gases which are set free afterwards, and the heavy gases are thus exposed to the white heat of the upper part of the retort. If, however, according to the proposal of Vivian B. Lewes, producer-gas is introduced into the gas-retort, such a dilution takes place at once which will produce a smaller quantity of tar, which is, however, richer in oils.

Börnstein has also worked on the formation of tar from coal at comparatively low temperatures (*Chem. Zeit.*, 1904, 927; *Z. Elektrochem.*, 1904, 1863; *J. Gasbeleucht.*, vol. xlix., pp. 627, 648, 667; *Ber.*, 1906, 1238). When coal is slowly heated up to  $450^{\circ}\text{C}$ ., neither aromatic hydrocarbons nor phenols are formed, but methane homologues and pyrocatechine. In that case coals from more recent strata yield tars below the specific gravity of water, older coal-tars heavier than water. The gas produced at the same time contains but little free hydrogen, most of which is formed at higher temperatures by the decomposition of methane homologues and the formation of aromatic hydrocarbons. The tar produced below  $430^{\circ}$  from coal contains some of the higher ("hard") paraffins; also isomethylantracene and a hydrocarbon corresponding to "cracken,"  $\text{C}_{24}\text{H}_{18}$ .

*Influence of the shape of the Retorts.*—Even when the distillation of coal is carried out at higher temperatures for the purpose of making ordinary coal-gas, the composition of the tar may vary very much according to the shape of the retorts used, which causes the vapours to have more or less action on the hot material of the retort. This is proved by experiments made with Bueb's vertical retorts, which have recently attracted a great deal of attention (*Ger. P.* 167367; *J. Gasbeleucht.*, 1905, 833; 1906, 259, 325; *Z. Verein. deutsch. Ingen.*, 1906, 198). At Warsaw, where Bueb retorts were working alongside of the

ordinary horizontal retorts, the same coal yielded quite different tars with both, as shown here :—

	Vertical retorts.	Horizontal retorts.
Specific gravity of tar, about . . . . .	1.1	1.2
Free carbon . . . . .	2 to 4 %	about 20 %
Water . . . . .	2.17	3.5
Light oil . . . . .	5.85	3.10
Middle oil . . . . .	12.32	7.68
Heavy oil . . . . .	11.95	10.15
Anthracene oil . . . . .	15.96	11.64
Pitch . . . . .	49.75	62.00
Loss . . . . .	2.00	2.03

The tar from vertical retorts contains almost 50 per cent. less naphthalene than that from horizontal retorts.

Hayes (Silliman's *Amer. J.*, March 1859) had long before this made corresponding observations on the quality of the tar respecting the influence of the shape of the gas-retorts. Where the volatile products are carried away from the hottest place through a narrow pipe, much less heavy and more light oil are obtained, and the coke is more compact and harder.

These differences are evidently connected with variations of the *pressure* within the retort. At a higher pressure the gas cannot escape so quickly, and remains a longer time in contact with the hot walls of the retort, which produces secondary decomposition, as proved by the carbon secreted on the retort-walls and in the liquid distillates. This fault is corrected by the employment of exhausters (*cf.* p. 43).

The Tarless Fuel Syndicate (*The Engineer*, 1910, p. 230) erected at Battersea, according to the plans of W. S. Simpson, an experimental station for gasifying coal in a high vacuum. It was found there that the evolution of gas was much more rapid and the yield of by-products much higher than otherwise, the quantity of fixed carbon left behind being the same. Whereas the ordinary time for distilling bituminous slate is from 16 to 27 hours, the time at the vacuum plant is only  $1\frac{1}{2}$  to 2 hours. The latter yielded 134 gallons of oil (tar) per ton, against 90 gallons in the ordinary process.

Burstall (B. P. 18148, 1910) treats coal in air-tight retorts at a temperature of 800° to 1000°, and a reduced pressure (10 to 18 inches below atmospheric pressure), whereby he obtains

tar containing a high percentage of oils possessing a high inflaming point, some of which have a higher specific gravity than water. The tar thus obtained, according to W. G. Moore's B. P. 23376, 1910, yields on distilling between 32° and 316° C. from 40 to 45 per cent. oils; above that temperature come heavier products, and the residue remaining in the still is a black, wax-like substance which burns in the flame of the Bunsen burner with but slight evolution of smoke. The distillates separate themselves from one another by their specific gravities, so that one floats on the top of the other [?] and are of different colour. Towards the end of the distillation a substance of light-brown colour and tough consistency passes over. (Evidently in this kind of gasifying coal a product differing from all other descriptions of tar is formed. The formation of a non-miscible oily distillate has never previously been observed.)

Pictet and Bouvier (*Berl. Ber.*, 1913, p. 3342, and 1915, p. 926) describe the tar obtained by them by distilling coal (on a laboratory scale) at reduced pressure.

Of course, the *difference of the quality of the coal* used in gas-making (we here speak only of real coal, not of browncoal, etc., already referred to on p. 41) influences the composition of the tar. Newcastle coals furnish rich tar in naphthalene and anthracene. Among German coals, that from Silesia furnishes much better tar than that from Westphalia. According to Deville (*J. Gasbeleucht.*, 1889, 693), the percentage of *oxygen* in the coal has great influence in that respect. According to the variations of that constituent, he distinguishes the five following groups:—

	I.	II.	III.	IV.	V.
	5 to 6·5 % Oxygen.	6·5 to 7 % O.	7·5 to 9 % O.	9 to 11 % O.	11 to 18 % O.
Yield of tar . . . .	3·90	4·65	5·08	5·48	Per cent. 5·59
„ water . . . .	4·58	5·86	6·80	8·6	7·86
„ benzol in 1 cbm. of gas . . . .	26·67	37·02	35·96	38·94	Grams per cbm. 33·02

It is especially injurious to the quality of the tar if the lighting-power of the gas is augmented by addition of *boghead* or any similar *bituminous shales* to the coal. In such a case, even at the highest practical temperature, hydrocarbons of the paraffin series appear more extensively in the tar. The benzol then contains hydrocarbons similar to petroleum-spirit, and the anthracene paraffin, neither of which impurities can be removed by the methods usually practised, viz., fractional distillation or crystallization. Hence many tar-distillers stipulate in their contracts that the gas-works must not mix more than 5 per cent. of shale (boghead, etc.), with their gas-coal.

Besides paraffins, boghead tar contains principally toluene and naphthalene, and but little benzene and anthracene. The real boghead, or Torbane-hill mineral, is now practically exhausted; but that name is still used in commerce for shales of much inferior quality. The shale-spirit got from these contains, along with the paraffins, very sensible quantities of benzene and toluene.<sup>1</sup>

Through the kind mediation of Professor Dittmar I have received the following information from Dr Ronalds on the tar from *cannel coals* and *boghead*. Scotch cannel were exclusively used in Edinburgh and Leith, and probably in most parts of Scotland, for making gas prior to the coal famine in 1851-53, when many companies took to using common splint coal, and some attempts were even made to use shale mixed with coal. Shales give little or no tar; and the naphtha (if *any*) is similar to that from boghead (the hydride series). The quality of the tar now made from the various kinds of cannel coal (such as those from Lesmahagow, Marquis of Lothian, Arniston, Benhar, Wallyford, and numerous other localities) is very different from that obtained formerly. Formerly, when *low* heats were used at the gas-works, as much as 8 per cent. of naphtha (*i.e.* benzene and its homologues) was obtained by distillation with steam. This diminished slowly as the heat employed at the gas-works increased, until it had fallen to about 3 per cent. The naphtha from Scotch tar was always rich in toluene, and contained less benzene than that from ordinary bituminous coal. It contains little naphthalene and very little anthracene—so little of the latter that its extraction

<sup>1</sup> Watson Smith, private communication.



is not worth while. It also contains considerable quantities of paraffins, but mostly of low melting-points. Naphthalene and paraffin seem to go together; wherever there is much of the one, the other is almost always present too.

Dr Kraemer (priv. comm.) regards the notion that solid paraffin occurs in real coal-tar, as erroneous. In his opinion, solid paraffin only appears whenever cannel coal, or shale, or similar substances have been employed along with real coal; and the reason why naphthalene and paraffins generally occur together is simply this, that coals yielding much naphthalene usually require an addition of the above-mentioned substances in order to produce good gas. (It should be noticed that the different experience of Dr Ronalds had been gained with another material, viz., Scotch cannel coals.)

When shale or boghead or similar semicoals are mixed with cannel or bituminous coal, the light naphtha is a mixture of the benzene and of the methane series; as these are very difficult to separate, the benzol is comparatively valueless as a commercial product. The heat used in the making of the gas and tar appears to have quite as much, if not more, to do with the quality of the products as the quality of the coal has.

A special investigation by Dr Bunte<sup>1</sup> shows the influence of the quality of coal on the quality and quantity of gas, tar, and ammonia produced in distillation. We extract from it the following statements (partly translated into English measures). The five descriptions of coals distilled had the following composition:—

Description of Coal.	Total contents of the Coal.					Composition of the organic substance.		
	C.	H.	O (+N & S).	Water.	Ash.	C.	H.	O (+N & S).
Westphalian (Consolidation) . .	78.94	5.22	7.59	1.64	6.62	86.04	5.69	8.27
Saar (Heinitz I.) . .	77.18	4.97	9.27	2.00	6.48	84.44	5.43	10.73
Bohemian (Thurn and Taxis) . .	71.97	5.36	10.18	5.61	6.88	82.15	6.12	11.64
Saxon (Zwickau) . .	68.75	4.91	11.05	7.79	7.50	81.16	5.80	13.04
Bohemian cannel coal (Pilsen) . .	67.41	5.98	8.87	3.33	14.43	81.95	7.27	10.78

<sup>1</sup> *J. Gasbeleucht.*, 1886.

These coals, when distilled in an ordinary gas-retort, fitted up with special condensing-apparatus for experimental purposes, but otherwise working under normal manufacturing conditions yielded for each 100 kg. of coal the following products:—

Description of coal	Coke, kil.	Gas.				Temperature of retorts, °C.	Tar, kil.	Ammon. liquid, kil.	Loss, kil.
		Kil.	Cubic metres.	Cubic feet, per ton.	Illum. power candle.				
Westphalia	71.4	16.95	30.33	11,899	11.15	1360-1385	4.09	4.44	3.12
Saar. . .	68.3	17.71	30.18	11,835	10.27	1205-1290	5.33	6.90	1.76
Bohemia .	63.3	18.52	28.47	10,221	10.20	1240-1350	5.79	9.06	3.33
Zwickau .	62.7	15.81	25.46	9,140	10.59	1180-1240	5.22	11.89	4.38
Boh. cannel	56.3	25.72	30.38	11,916	18.17	1180-1350	8.81	6.45	2.72

This seems to show that the quantity of tar increases with the percentage of oxygen in the coal, apart from the necessarily different case of cannel coal. The increase of the yield of ammoniacal liquor is in the same direction; but this proves nothing, as neither the strength of the liquor nor the original percentage of nitrogen in the coal is stated.

Bunte's results have been completely confirmed by the report of the 1012 trials made, on a working scale, by the Paris Gas Company from 1874 to 1884, with 59 different classes of coal.<sup>1</sup> The conclusions arrived at are:—"The higher the percentage of oxygen, the more tar and ammonia is formed and the more hygroscopic water is contained in the raw coal; on the other hand, the yield of coke and gas is less with a rise in the percentage of oxygen." Bertelsman (*loc. cit.*, p. 23) does not allow this conclusion to be final, since there are too many exceptions to the rule.

Other communications on this subject have been made by Spilker (*Kokerei und Teerprodukte der Kohle*, p. 23); Constam, Schläpfer, and Kolbe (*J. Gasbeleucht.*, 1906, p. 741; 1908, p. 669; 1909, p. 770); Peters (*J. Gasbeleucht.*, 1908, p. 1114).

American coal-tars are stated by White and Hess (*J. Soc. Chem. Ind.*, 1900, 509) to be inferior to European tar as regards the recovery of benzol, etc., but they are rich in anthracene. They give a number of analyses.

<sup>1</sup> *J. de Pélclairage au Gaz*, juillet, 1886.

An interesting paper has been published by Porter and Ovitz (*J. Amer. Chem. Soc.*, 1908, pp. 1486 *et seq.*) on the "Nature of the Volatile Matter of Coal," as evolved under varying conditions. As the contents of that paper do not bear in any direct way on the matter treated in this book, we must confine ourselves to drawing attention to it.

Of course the *duration* of the distilling-process and (what is intimately connected with this) the *weight of the single charges* greatly influence the yield of tar. On this point investigations have been made, amongst others, by Rau (*loc. cit.*), Spilker (*Ammoniakbildung*, Aachen, 1905), Bury (*J. Gas Lighting*, 1907, p. 982).

#### *Yield of Tar from the Coal.*

In Germany this is set down to average 5 per cent. on the weight of the coal.

Drehschmidt (*J. Gasbeleucht.*, 1904, p. 677) obtained with gas-coal yielding 58 to 75 per cent. coke, from 3 to 9 per cent. tar; Bunte (*ibid.*, 1909, p. 725) with gas-coal yielding 59 to 71 per cent. coke, from 4 to 5 per cent. tar. Ott (*ibid.*, 1909, p. 591) found no difference in the yield of tar, whether working with horizontal or with upright retorts.

Wanklyn (*Gas Engineer's Chemical Manual*, p. 5) states that one ton of coking-coal (Newcastle coal) yields:—

	Lbs.	Per cent.
10,000 cubic feet of gas . . . . .	380	17.0
10 gallons of tar . . . . .	115	5.1
Virgin gas-liquor * . . . . .	177	7.9
Coke . . . . .	1568	70.0
	<u>2240</u>	<u>100.0</u>

\* That is, the liquor condensing from the gas alone without any water running down within the scrubbers.

Exact figures concerning the yield of tar in London and provincial gas-works have been given on pp. 44 and 45. According to Wurtz,<sup>1</sup> St Etienne coal only yields 4 per cent. of poor tar, but Anzin and Mons coal 6.73 per cent., and "Prussian" coal up to 7 per cent., of rich tar. Of the German coals those from Upper Silesia yield the best, those from Westphalia the poorest tar. The yield of tar is given in the following table,<sup>2</sup> which

<sup>1</sup> *Dictionn. de Chimie*, i., p. 1631.

<sup>2</sup> Stohmann-Kerl's *Chimie*, 3rd ed., p. 624.

shows that from various descriptions of coal, along with that of other products, on the average there is obtained :—

	Tar.	Ammoniacal liquor.
From coal generally . . .	4 to 6	6 to 10 per cent.
„ English coals . . .	4.5	6 „
„ Silesian „ . . .	5 to 6	9 „

1 ton (2240 lb.).	Gas.		Coke.	Tar.	Gas-liquor.	Loss.
	Cub. ft.	Lb.	Lb.	Lb.	Lb.	Lb.
Boghead cannel . . .	13,334	...	715	733.3	...	...
Newcastle . . .	9,833	...	1426	98.3	60	...
Wigan cannel . . .	10,850	...	1332	218.3	161.9	...
Lochgelly . . .	8,331	...	1245	225	340	...
$\frac{1}{2}$ Lochgelly + $\frac{1}{2}$ Boghead .	9,055	...	1200	400	170	...
$\frac{1}{4}$ „ + $\frac{3}{4}$ „ . . .	9,050	...	1205	335	290	...
$\frac{1}{4}$ „ + $\frac{3}{4}$ „ . . .	9,750	...	1240	227	270	...
Pelton Main (Durham) .	9,500	...	1540	112.5	112.5	...
$\frac{1}{2}$ „ + $\frac{1}{2}$ Boghead . . .	12,300	...	1366	206.6	116.6	...
Lesmahagow cannel, I. .	11,681	461	1091	594	4.5	87.5
„ „ II. . .	9,878	483.5	1064	603	4.5	85
Ramsay's N'castle cannel	9,016	410	1435	295	6.7	93.3
Derbyshire deep-seam .	9,400	300	1335	219	179	207
Wemyss cannel, I. . .	10,976	551	1124.5	224	...	340
„ „ II. . .	10,192	528	1188	197	...	327
Wigan cannel . . .	9,408	338	1326	250	...	326

The following statements (Muspratt-Stohmann's *Chemie*, 4th ed., v., p. 319) summarize the results obtained at 67 German gas-works in 1891-92, working with gas-coal proper, without additions of boghead, etc.:—

100 kg. Coals yield :—	Gas, cubic metres.	Coke, killog.	Tar, killog.
Westphalian coal . . .	$\overbrace{24.8-31.9}^{28.6}$	$\overbrace{59.1-76.0}^{66.0}$	$\overbrace{3.4-5.5}^{4.4}$
Saar coal . . .	$\overbrace{26.1-31.3}^{29.5}$	$\overbrace{60.0-71.0}^{64.9}$	$\overbrace{4.8-6.9}^{5.9}$
Silesian coal . . .	$\overbrace{24.4-31.2}^{28.3}$	$\overbrace{59.5-74.1}^{65.9}$	$\overbrace{3.8-6.0}^{4.9}$
Zwickau coal . . .	$\overbrace{26.4-29.5}^{27.64}$	$\overbrace{54.2-57.6}^{55.3}$	$\overbrace{4.7-6.3}^{5.6}$
English coal . . .	$\overbrace{26.4-30.8}^{28.6}$	$\overbrace{64.7-73.1}^{68.5}$	$\overbrace{4.0-5.9}^{4.8}$

For American coals Rau (*loc. cit.*) states the yield of tar at gas- and coke-works in 1904 at 3.34 to 6.79; average, 4.67 per cent.

*Proposals for Increasing the Quantity or Improving the Quality of Tar in the Manufacture of Coal-gas.*

We have already seen that both the quantity and the quality of tar differ with the quality of the coal and the temperature of distilling it, no doubt also with the pressure existing in the retort and the velocity with which the gases are evolved and are made to escape from the retorts. All these conditions, however, must in the first instance be made subservient to the aims of manufacturing illuminating-gas; that is, obtaining the best yield and the best quality of gas, the tar being left to take its chance. Still it may be possible to introduce such improvements as will serve the purpose of improving the yield or the quality of the tar, and the following proposals have been made with this object:—

H. Aitken (B. P. 4644, 1883) considers that the large amount of water contained in certain kinds of coal, shale, and lignite (real coal does not contain much water) causes the coke to be too porous and light, and carries off much of it in the unburnt state. He therefore dries the coal in a tower by drawing or blowing heated air or hot products of combustion through it. The coal thus treated is stated to yield much closer and heavier coke, a higher yield of gas, and tar containing more benzene. [Although this process might do for very moist materials, it would certainly not pay in most ordinary cases.]

N. A. H  louis, of Paris, evidently inspired by the reading of Berthelot's and other great savants' researches, but without much regard to the conditions and requirements of practical work, obtained provisional protection (B. P. 5142, 1083) for a process based on the "rational and permanent production of acetylene." This is to be attained: (1) by a fixed temperature never exceeding a dull red-heat in the retorts [!]; (2) by the permanent action of a current of previously superheated gas and steam led into the retorts during the whole time of the distillation; (3) by maintaining a mean pressure of  $\frac{1}{2}$  atmosphere in the

retorts. Thus acetylene, the [hypothetical] generator of benzene, is to be permanently produced, whilst the benzene itself is protected against being condensed into more complex carburets, constituting heavy oils of less commercial value.

Heusser (Ger. P. 24728) also from purely theoretical considerations on the "condensing" action of acids, zinc chloride, etc., believes it possible to obtain at will hydrocarbons of a lower boiling-point by passing chlorine gas and hydrochloric-acid vapour into the gas-retorts; and hydrocarbons of a higher boiling-point by mixing the coal with zinc chloride, with or without the admixture of tar or tar-oils, and also passing hydrochloric-acid vapour into the retorts during the dry distillation. It does not seem necessary to criticise this process.

Byrom, Wigan, and Bennett (B. P. 3736, 1884) propose removing the various products of distillation from the retorts before they are mixed, thus avoiding the expense of redistillation. This is to be done by providing the retort with a number of openings along its highest part, each exit-pipe being supplied with a bend which may be inclined downwards; the pipe being of sufficient length to secure the condensation of the liquid, the gases to be drawn off by an exhaustor. This process, if at all feasible, would evidently apply more to the distillation of shale, etc., for paraffin oil than to that of coal for gas-making.

Kunath (*Chem. Zeit.*, 1885, p. 1893) attributes the thickening of tar not merely to the presence of particles of coal carried over mechanically with the gas, but principally to a local superheating of the gas. Thinner tar is to be obtained by charging the retorts with as much coal as possible, and thus reducing the gas-space and the contact surfaces.

J. Young (B. P. 14840, 1886) mixes the coal before carbonizing with common salt in proportions varying with the composition of the coal, usually 4 lb. per ton of coal, in order to improve the quality of the coke, to facilitate the purification of the gas, and to increase the yield of gas, tar, and ammonia.

Dvorkovich (*J. Soc. Chem. Ind.*, 1893, p. 403) considers the present way of manufacturing gas as irrational. The coal is

better carbonized at a low temperature in the presence of an inert gas (carbon monoxide, hydrogen, or water-gas); in this case a large quantity of "coal-oil" passes over, similar to petroleum residues, which is to be split up by overheating into more gas and aromatic hydrocarbons, as effected by Letny and Ragosine (see below).

We shall later on meet with several other attempts at improving the quality of the tar or increasing the quantity of its more valuable constituents by a special treatment while in the gas-retorts or subsequently.

Recent patents for improvements in the recovery of tar in the process of gas-making:—

Smith and Allbright (B. P. 9070, 1902).

Holmes (B. P. 20677, 1903).

Planting (Ger. P., appl. P13626).

Everitt (B. P. 13316, 1904).

Several inventors employ *steam*, either in the retorts or upon the gas after leaving them, for the purpose of facilitating the precipitation of the tar (and some ammonia) on cooling. Thenius recommended this many years ago (Wagner's *Jahresber.*, 1865, p. 738). Recent patents on this line:—

Heinemann (Ger. P. 138250).

Burgemeister (Ger. P. 154028).

Th. von Bauer (Ger. P., appl. B36982), for coke-ovens.

### *Recovery of the Tar suspended in the Gas.*

Ordinary coal-gas always contains a good many tarry particles in mechanical suspension. These particles are to some extent precipitated in the gas-pipes, and are found both at the gas-works and in the "siphons" (traps) of the street pipes as oils or as masses of crystallized naphthalene. These oils have been examined in detail by Gasch.<sup>1</sup> He found that they gave off—

3 to 6 per cent.	up to 100°,
5 " 8 "	from 100° to 180°,
5 " 15 "	" 130° " 150°,
19 " 36 "	" 150° " 180°,

<sup>1</sup> *J. Gasbeleucht.*, 1873, p. 65; Wagner's *Jahresber.*, 1873, p. 914.

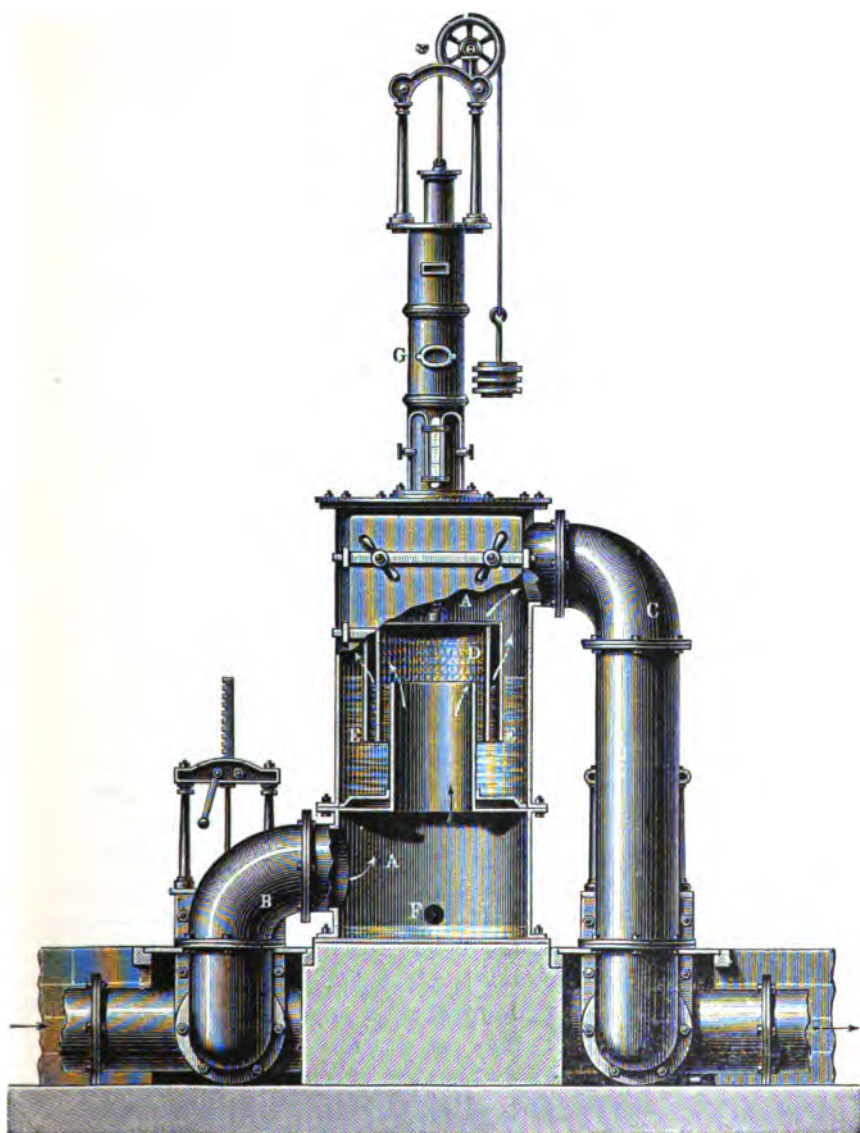


FIG. 2.



on the whole 47 to 76 per cent. up to the points where naphthalene appeared. They contain numerous sulphur compounds—below  $100^{\circ}$  carbon bisulphide, above  $100^{\circ}$  probably thiophene. An exact examination of these oils (which do not appear to be systematically collected anywhere) is still wanting.

The quantity of tar can be considerably increased by supplementing the condensing-action of the air-condensers and scrubbers by more efficient apparatus. This is the object of the process of Pelouze and Audouin,<sup>1</sup> which is being worked very successfully at Paris and elsewhere. That they are not the real inventors of the process has been decisively proved by Colladon.<sup>2</sup> The invention proceeds from the principle that mere cooling cannot possibly condense all the tar, because the latter remains mechanically suspended in the gas in the shape of extremely minute liquid drops, *i.e.* in the form of a mist. A portion of this is retained in the coke-scrubbers, but very far from all of it. The result is different when the gas is made to issue through narrow apertures and impinge against a broad solid surface, over which it must spread. The fine liquid particles, thus brought into very much increased contact with each other and with solid bodies, gather into larger drops, and are thus retained. Fig. 2 (p. 57) shows how this principle is carried out. The gas passes into a vessel, A, through the inlet-pipe B, and leaves it at C. Inside A is a cylinder, D, the proper purifying-apparatus, which floats in the hydraulic tar-lute E, so that the gas can only get from B to C through the perforated sides of D. The latter are made of three concentric sheets of brass,  $\frac{1}{8}$  inch apart, and perforated with many holes. The holes *a a* (Fig. 3),  $\frac{1}{8}$  inch wide, are arranged in three rows placed transverse to each other. The jets of gas, issuing through the holes of the innermost plate, meet with the solid portion of the middle plate, and when issuing through the holes of the latter again meet solid portions of the outermost plate, from which at last they can get into the upper space of B. Since experience has shown that the holes of the middle plate especially are readily clogged up with tar, the apertures of this plate are now made (as shown in Fig. 3) larger and square. It has also been attempted to replace the holes by vertical slits,

<sup>1</sup> *Comptes rend.*, lxxvi., pp. 264, 928.

<sup>2</sup> *Ibid.*, lxxvii., p. 819.

which do not so easily get stopped up. The tar condensed by the impact on the plates runs into the tar-cistern E, flows over and runs away at F. Since of course some pressure is lost in this apparatus, it is necessary to let the gas, previously well cooled, issue under a certain surplus pressure, say  $1\frac{3}{4}$  to  $1\frac{7}{8}$  inch, which is kept constant by the automatic regulator G.

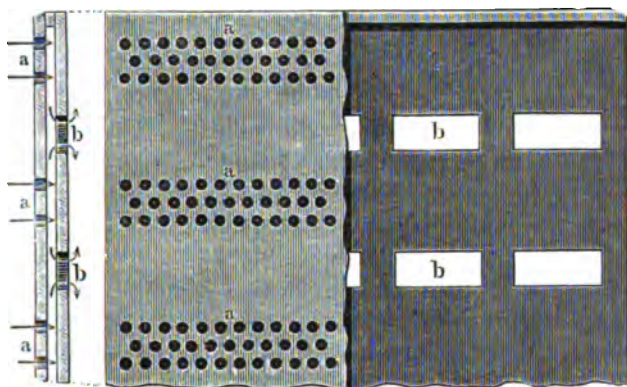


FIG. 3.

In 1876 there were eight such condensers at work in Paris, which produced:—At the Ternes works, from 1000 cbm. of well-cooled gas, 9 kg. of tar; at the La Villette works, from 1000 cbm. of gas not so well cooled, as much as 72 kg. of tar, and 16 litres of liquor containing 80 g. of ammonia per litre. The tar is much lighter than ordinary gas-tar; it yields 20 per cent. of light oils, instead of 3 to 5 per cent.

This apparatus is employed at many French gas-works, and it has also been introduced into other countries, for instance, into Germany. At first the objection was made to it that it is very difficult to keep the holes from being clogged up, and that it is doubtful whether the extra yield of tar is not counter-balanced by the loss in the illuminating-power of the gas. But, as a matter of fact, the apparatus has been in full work at quite a number of gas-works outside of France up to the present time, and during the last few years it has also been introduced in quite a number of Westphalian coke-works for recovering the tar from coke-oven gas.

Other apparatus, on the same principle, has been patented by Fr. Lux (Ger. P. 40897). It is a closed box, in which undulated metal sheets are placed in such a way that two adjoining sheets always form a chamber, with a number of compartments.

On the same principle is constructed the apparatus of Servier (*J. Gasbeleucht.*, 1880, p. 639). The same object, together with scrubbing the gas by water, is pursued by the inventions of Chevalet (*J. Gasbeleucht.*, 1883, p. 420), Fleischhauer (*ibid.*, 1887, pp. 27 and 1020), and Schumann & K  chler (Ger. P. 67767); also by Drory's tar-scrubber, perhaps that apparatus which is most employed at the present time and by which upwards of 90 per cent. (sometimes 99 per cent.) of the tar and 20 per cent. of the ammonia is taken out of the gas.

Scheibe (Ger. P. 184038) employs a fan-blast; by the impact of the gas against the outer shell, the liquid (and solid) particles are made to adhere to this, until they flow downwards, where they are constantly removed.

The Gasmotorenfabrik Deutz (Ger. P. 183823) employs a number of chambers superposed over one another, with impact surfaces inside, the shock against which causes the precipitation of the tar.

The Berlin-Anhaltische Maschinenbau Aktien Gesellschaft (Ger. P. 183413) employs revolving drums, placed in superposed chambers, with brushes in the intermediate space. The drums dip into the dish-shaped bottoms of the chambers. Another tar-separator is described in the Ger. Ps. 282279 and 284971 of the same firm.

Ott (Ger. P. 183519) also employs a system of superposed chambers, with impact surfaces.

Koppers (priv. comm.) has improved the Pelouze-Audouin apparatus by attaching overflow pipes to the outside box, whereby the level of the liquid can be changed at will, and by employing, in lieu of a single bell, four bells with as many inlet tubes, so that a more or less large space can be provided for the gas-inlet. His apparatus is shown in Figs. 4 and 5 (p. 61).

H. F. Smith (U.S., P. 1140198) removes the tar from gas by passing the gas through glass-wool fabrics or other pervious diaphragms.

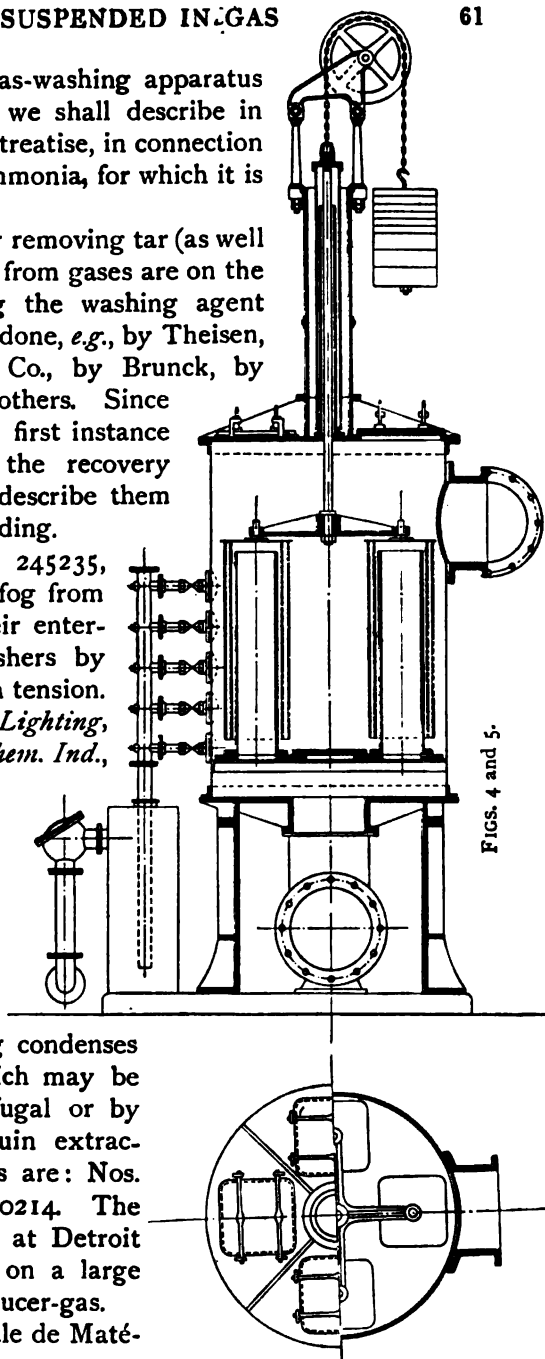
A very important gas-washing apparatus is that of Feld, which we shall describe in the second part of this treatise, in connection with the recovery of ammonia, for which it is primarily intended.

Other inventions for removing tar (as well as dust, ammonia, etc.) from gases are on the principle of converting the washing agent into a spray. This is done, *e.g.*, by Theisen, by Louis Schwarz & Co., by Brunck, by Dr C. Otto & Co., and others. Since they are usually in the first instance intended to increase the recovery of ammonia, we shall describe them later on under that heading.

Püning (Ger. P. 245235, 1910) removes the tar-fog from gases previously to their entering the ammonia washers by electric currents of high tension.

Steere (*J. Gas Lighting*, 1914, p. 309; *J. Soc. Chem. Ind.*, 1914, xxxiii, p. 1145) removes the tar from crude coal-gas or producer-gas by an alternating high-tension discharge at 40,000-80,000 volts, preferably at temperatures from 65° to 80°; the tar-fog condenses to large globules, which may be removed by a centrifugal or by a Pelouze and Audouin extractor. His U.S. patents are: Nos. 1130212, 1130213, 1130214. The Ford Motor Company at Detroit employs this process on a large scale for purifying producer-gas.

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FIGS. 4 and 5.

riel à Gaz (Fr. P. 469302) removes tar, etc., from gases by means of a horizontal cylinder, divided into two compartments by a horizontal partition having an opening at its centre. The gas is introduced tangentially through an inlet at the periphery of one compartment, travels with increasing velocity to the centre, and passes through the opening into the other compartment, wherein its velocity decreases from the centre to a tangential outlet at the periphery. Two or more such cylinders may be used in series. Each compartment is provided with a drain-pipe for discharging the separated tar.

White, Rowley, and Wirth (*J. Gas Lighting*, 1914, cxxvii, p. 719) pass the gas, after leaving the Pelouze and Audouin tar-separator, at the rate of 24,000 cub. feet per hour through an 8-inch pipe, of the shape of an inverted U, with electrodes of sixteen 27-gauge steel wires strung between 4-inch iron disks, 5 ft. 8 in. apart, through which a current of 20,000 volts is maintained; thereby the tar is completely removed.

Körting Brothers (Ger. P. 204888) put gas-tight iron tanks for the condensed tar and ammonia into connection with a pipe conducting coal-gas into the tanks, in order to prevent the entrance of atmospheric air, which would cause corrosion of the iron.

G. T. Purves (*J. Soc. Chem. Ind.*, 1915, p. 328) advocates the fractional collection of coal-tar at gas-works, especially with the object of removing the tar-fog from the gas, and suggests special tar-condensing plant for this purpose. He employs the "Otto" tar-spray as being by far the best apparatus.

S. Carter (*J. Gas Lighting*, 1915, p. 89; *J. Soc. Chem. Ind.*, 1915, p. 481) for the same purpose recommends the "Hurricane" tar-trap. Previous filtration of the gas under vacuum is more satisfactory than under pressure, as then the gas is not dried unduly.

#### *Estimation of the Tar contained in Gases.*

Such an estimation would be especially useful where it is the question of controlling the efficiency of a condensing process. Before the gas in the direct carbonizing process gets to the sulphuric acid saturators and to the benzol washers, it should be free from tarry particles.

Until quite recently, we did not as yet possess a reliable

method for the quantitative estimation of tar in gases. The ordinary way of proceeding is: to interpose in the gaseous current a weighed glass tube filled with loose cotton-wool, which is supposed to retain the tar. More accurate is the process of Tieftrunk, in which the gas is thoroughly washed with dilute alcohol (25 to 30 per cent.). The alcoholic solution is allowed to evaporate in a weighed vessel at the ordinary temperature; to the weight thus found one-third is added to allow for the light tar-oils, especially benzene and toluene, which escape during the evaporating of the alcohol. This is, however, a very inaccurate process, and it takes, moreover, considerable time until a constant weight is obtained. For small quantities of tar contained in the gas it is quite useless.

Feld (*J. Gasbeleucht.*, 1911, p. 33) has worked out another method which is both rapid and reliable. The tar is retained, as in the last-mentioned method, in a dry, weighed U-tube, filled with loose cotton-wool. In order to avoid as much as possible the retention of the water contained in the gas, the U-tube is placed in a vessel filled with water, or another liquid kept at about the same temperature as the gas. The U-tube should be well insulated in order to keep the temperature as constant as possible. At the end of the experiment some dry gas, the same as is being examined (not air!), is passed through the tube in order to dry its contents. For this object, at the end of the experiment two U-tubes are placed in front of the absorbing-tube, and these are equally placed in the heated liquor. The first U-tube is filled with cotton-wool, the second with calcium chloride; the third is the tube in which the test is performed. The first of these U-tubes retains the tar contained in the gas, the second retains the water from the same. Since the gas employed for drying is now saturated at the temperature of the experiment with the same tar-constituents as are contained in the test-tube, the gas now does not take up from the latter any tar constituents, but only water. A constant weight is generally attained when a little more gas than that previously used for the test has been passed through.

Gwiggner (*Chem. Zeit.*, 1912, p. 462) describes an apparatus for estimating the tar in gases, especially producer-gases.

*Recovery of Benzol contained as Vapour in Coal-gas.*

It has long been known that a good deal of benzol and its homologues is contained in coal-gas, and adds much to its illuminating-power. According to the extensive experiments made by the Paris Gas Company, the percentage is pretty constant in the case of the various descriptions of coal, and amounts for 1 cbm. of gas to 30 g. of benzene and 9 g. of toluene, etc.; by volume to 1.05 per cent., along with 5.5 to 4.8 per cent. by volume of heavy hydrocarbons belonging to the aliphatic series. The benzene, etc., separates in the liquid state when cooling down the gas to  $-70^{\circ}\text{C}$ ., whilst the other heavy hydrocarbons remain in the gaseous state. From this we may make the following calculation:—One ton of coals yields about 11,000 cub. ft., or, say, 300 cbm. of gas, containing 11.7 kg. of benzol, etc. At the same time about 1 cwt. of tar is formed, from which about 0.5 kg. of benzol is obtained. *Hence coal-gas in this case contained 23 times as much benzol as the tar formed from the coal at the same time*; and this is a very legitimate stimulus for attempts to recover benzol from coal-gas.

St Claire-Deville (*J. d. Us. à Gaz*, 1889), by cooling down the gas to  $-70^{\circ}\text{C}$ ., obtained from 1 cbm. of Paris gas 35.48 g. of aromatic hydrocarbons, containing:—

Benzene, boiling-point $81^{\circ}$	.	.	.	73.13 per cent.
Toluene, „ 111°	.	.	.	13.00 „
Xylene and higher homologues, boiling-point $139^{\circ}$	.	.	.	8.75 „
Residue and loss	.	.	.	5.12 „

In Bunte's investigation at the Karlsruhe gas-works (*J. Gasbeleucht.*, 1894, p. 601), 100 kg. of coals yielded:—

1. 30.0 cbm. = 17.04 kg. of gas, containing 938 g. benzene (95 per cent. of the total  $\text{C}_6\text{H}_6$ ), and 312 g. toluene (89 per cent. of the total  $\text{C}_7\text{H}_8$ ), with traces of naphthalene.
2. 5 kg. of tar, containing 5 g. benzene (= 5 per cent.), 40 g. toluene (= 11 per cent. of the total  $\text{C}_7\text{H}_8$ ), 300 g. naphthalene, 70 g. phenol, 20 g. anthracene.
3. 11 kg. ammoniacal liquor.

Further investigations by Bunsen (*Gasometer. Methoden*, 1877), Berthelot (*J. Gasbeleucht.*, 1876, p. 409; 1877, p. 525),

Knublauch (*ibid.*, 1880, p. 256), Dennstedt and Ahrens (*Berl. Ber.*, 1894, p. 601), whilst confirming the large proportion of benzene and toluene contained in the gas in the state of vapour, do not make it out quite as high as the first Paris investigation. As final result we may state that *there is about 15 times as much benzene and toluene vapour in the gas as is contained in the tar formed at the same time.*

The percentage of benzol in *coke-oven gases* is decidedly smaller than in ordinary coal-gas made for illuminating purposes (which can be easily understood, since the quality of coal used for coke differs from that used for illuminating-gas). Kraemer (*Glückauf*, 1897, p. 381) estimates the quantity of benzol in coke-oven gas at half of that in illuminating-gas. In 1900 the Westphalian factories obtained an average yield of 0.4 per cent. benzene and 0.09 per cent. toluene on the coal coked; the Laar works averaged 0.9 to 1 per cent. (Haarman, *loc. cit.*, p. 28).

S. Mellor (B. P. 5604, 1882) proposes to obtain benzol, toluol, or their homologues by *subjecting coal-gas to a pressure of 4 or more atmospheres*, whereby those hydrocarbons are deposited in a liquid form. This proposal is manifestly impracticable if it is intended to be applied to ordinary coal-gas. But it seems a different matter when we consider the "rich" gas obtained from petroleum, fatty oils, etc., and subjected to several atmospheres' pressures, in order to light railway-carriages and the like. In this case liquids are spontaneously condensed, and it needs only to be called to mind that Faraday, in 1825, discovered benzene in a liquid condensing from compressed oil-gas. Greville Williams (B. P. 4663, 1884) treats such liquids in the following manner:—They are distilled, and all coming over below 65°.5 is rejected. The second portion is collected between 65°.5 and 87°.5, the third portion above 87°.5. To separate benzene (toluene, etc.) from these distillates, they are subjected to the action of dilute nitric acid (100 gall. requires 50 gall. commercial nitric acid and 50 gall. water), or of a mixture of sodium nitrate and sulphuric acid (190 lb. commercial nitrate of soda, 218 lb. commercial oil of vitriol, and 24½ gall. water to 100 gall. oil). The mixture is then distilled in a salt-glazed stoneware still by means of a steam- or water-bath; benzene and its homologues readily come over, the homologues of olefant gas being converted into compounds, which remain behind in the



still. The scientific principles underlying this proposal have been discussed by Greville Williams in the *Chem. News*, vol. xlix., p. 197. He found that the liquid obtained in manufacturing the "Pintsch gas" contained from 65.6 down to 24.6 per cent. of benzene and toluene, according to its specific gravity, which varied from 0.850 to 0.760. It should be noted that any process involving the distillation of liquids containing a large quantity of free nitric acid, and then necessitating the use of stoneware stills, must present a good deal of inconvenience.

Armstrong<sup>1</sup> has also subjected to examination the liquids condensing from Pintsch gas and some other descriptions of compressed gas made from oil or petroleum. These liquids, commonly called "hydrocarbon," are practically free from paraffins; they essentially consist of benzene and toluene (rarely less than 50 per cent.), of the dimethyl- and trimethyl-benzenes occurring in coal-tar, of naphthalene, of the hydrocarbons of the olefine and "pseudo-olefine" series (viz, ethylene, propylene, amylene, hexylene, and heptylene), and the "pseudo-acetylene" series (especially crotonylene, dimethylene-ethane, and isoallyl-ethylene); also much cyclopentadiene. This "hydrocarbon," amounting to rather less than 1 gall. per 1000 ft. of compressed gas, is not used by tar-distillers, as it is too difficult to separate the benzene and toluene from the other hydrocarbons; it is exported to Belgium, where it is said to be used for varnish-making. Entirely different from this liquid is the "tar" depositing from the oil-gas prior to its collection in the gas-holder, and amounting to about 5 gall. per 1000 ft. of gas; it contains neither acids nor basic constituents, and little, or even hardly any, benzenoid hydrocarbons, but mostly undecomposed petroleum hydrocarbons—that is, the material started from.

Etard and Lambert (*Comptes rend.*, cxii., p. 495) examined the liquid condensed by compressing the rich gas made from paraffin oil, and found therein 60 per cent. benzene, 10 per cent. toluene, 6 per cent. non-saturated light and 10 per cent. ditto heavy hydrocarbons, boiling between 140° and 190°; moreover a hydrocarbon of the formula  $C_6H_6$ , boiling at 42°.5, easily polymerized in the cold, which they call "pyro-pentylene,"

<sup>1</sup> *J. Soc. Chem. Ind.*, 1884, p. 462; Armstrong and Miller, *J. Chem. Soc.*, vol. xlix., p. 74.

and which is probably identical with the "cyclo-pentadiene" discovered by Kraemer and Spilker in ordinary coal-tar (*Berl. Ber.*, 1896, p. 533).

According to Kraemer (priv. comm.), it is easy to separate the benzenoid hydrocarbons from the olefins by means of *free chlorine*, which combines with the olefins, so that benzol, etc., can be blown off. This process has been carried out in practice; but it is now supplanted by a still better one, consisting in a treatment with picric acid.

*Cooling* to a low temperature has also been proposed for the purpose of condensing hydrocarbons from coal-gas; but the objections to be made to this operation, if intended to apply to ordinary coal-gas, are quite obvious.

A second series of proposals employs the process of depriving either ordinary or specially prepared coal-gas of the particles of aromatic hydrocarbons suspended and contained as vapour in it, by *passing the gas through liquid absorbents* for those substances. A. Vogel<sup>1</sup> passed the gas through colza-oil, which thereby increased 20.5 per cent. in weight and very much in illuminating-power, whilst that of the gas did not suffer. The last statement is more than doubtful; it is now generally assumed that the illuminating-power of coal-gas is to a very great extent due to the presence of benzene vapours, the results of Berthelot<sup>2</sup> in this direction having been confirmed by many subsequent investigations of Frankland and other chemists. On the contrary, by removing the benzol from coal-gas, it becomes a "poor gas," unfit for illuminating purposes, unless "carburetted" again in some other way, *e.g.*, by the vapours from petroleum-spirit and the like, or else applied (as it had been already previously done with water-gas) on the principle of the "incandescent" light, namely by introducing some solid body, as platinum, magnesia, zirconium, etc., into the flame in order to give out light after having been raised to a white heat. That the light-giving constituents of coal-gas are almost entirely removed by passing it through heavy mineral oils was noticed in 1868 by Cusiter; but his observations were only made known to a very limited circle in 1874.<sup>3</sup>

<sup>1</sup> *Dingl. polyt. J.*, vol. cliii., p. 464.

<sup>2</sup> *Comptes rend.*, vol. lxxxiv., p. 571.

<sup>3</sup> Davis, *J. Soc. Chem. Ind.*, 1884, p. 432.

Whilst Vogel evidently did not aim at extracting benzol as such, this was the aim of a process devised by Caro, A. Clemm, C. Clemm, and Engelhorn (B. P. Feb. 17, 1869), during a period in which the price of benzol had risen enormously. They brought the gas into contact with oils of high boiling-points, such as petroleum, paraffin oil, or fatty oils, and separated the benzene and toluene absorbed by subsequent fractional distillation, so that the residual oil could be used over again as an absorbent. This process did not hold its ground for any length of time, the decline in the price of benzol and the reduction in the value of the gas making it unremunerative.

In 1875 J. Barrow patented the application of artificial refrigeration to the collection of the vapours of solvent naphtha evolved in the working of indiarubber, afterwards absorbing them in oil—an idea which has since been utilized for a similar treatment of the benzene vapours contained in coal-gas.

In 1882 Caro's idea was again taken up, first by J. Hardman (B. P. 4312, 1882), who began the process in the gas-retort itself, distilling at a very high temperature in order to produce more benzene and its homologues. These hydrocarbons are separated from the gas by means of condensing apparatus, which are charged with anthracene oil or other heavy hydrocarbons. The gas, after this treatment, is useless for illumination, and is only fit for heating purposes. We here meet with the idea that the manufacture of gas is to be treated as a secondary process, that of benzol being the primary object in view, to be promoted by a special treatment of coal.

A very similar course was taken by G. E. Davis (B. Ps. 5717, 1882; and 4468, 1883). He proposed ascertaining by experiment, for each particular kind of coal, the minimum temperature at which it will yield the maximum quantity of benzol without forming paraffins. This would be a lower temperature than in ordinary gas-making, and only 7000 to 8000 cub. ft. of gas would be obtained from each ton of coal. Before charging into the retorts, the coal is to be moistened with some of the concentrated spent ammonia-water containing the sulphocyanides, so that the temperature of the retort is lowered and more ammonia is obtained. The gas is then washed or scrubbed with water, previously warmed to diminish its power of dissolving hydrocarbons and hydrogen sulphide. It is then passed

through a weak acid or other substance capable of retaining the ammonia, and is then purified, as usual in gas-works, from cyanides, sulphocyanides, and part of its hydrogen sulphide, leaving some of the latter purposely unabsorbed, as it is wanted afterwards. Now comes the operation interesting us most here:—The gas is passed, at as low a temperature as possible (producing this by an air-cooling or freezing-machine, or else by the expansion of the gas after previously compressing it), through a hydrocarbon oil boiling at a high temperature. It thereby loses most of its illuminating-power, and is only used as fuel for heating the retorts. In this process the  $H_2S$  previously left in is burned into  $SO_2$ . The products of combustion are brought into contact with ammonia-gas or ammonium carbonate, obtained by heating the ammoniacal liquor previously formed, whereby ammonium sulphite is produced, part of which is oxidized by the excess of air into sulphate. The inventor states that he thus obtained from 1 ton of coal, at a temperature of about  $650^{\circ} C.$ , 16 gall. of tar, 37 gall. of ammoniacal water, 11 lb. of sulphur,  $12\frac{1}{2}$  cwt. coke, and 7000 cub. ft. of gas, which gave 4 gall. of benzol testing 90 per cent. at  $100^{\circ} C.$  The gas can then be used for heating purposes, or it can be used for lighting by means of some "carburetting" process.

A detailed description of Davis's process, and an analysis of the crude benzol obtained, is found in the *Journal of the Society of Chemical Industry*, 1883, p. 522. He admits there that the loss of absorbing-oil is greater than at first anticipated, and that the process will only pay with benzol at a certain price, which was then easily obtainable (4s. to 5s., or at least 3s. per gallon), but which is out of the question at the present time. It is also evident that such a lowering of prices, if it had not occurred from other causes, would have been the inevitable consequence of any large extension of the process. In the discussion of Davis's paper it was stated that it takes all the gas produced, and 1 cwt. of coke in addition per ton of coal, to heat the gas-retorts.

E. Drew (B. P. 5039, 1883) proposed certain mechanical arrangements for treating the gas with heavy hydrocarbon oils. Another patent of the same inventor (No. 5505, 1883) prescribes treating the gas with such oils in a highly compressed state.

Levinstein (*J. Soc. Chem. Ind.*, 1883, p. 217) points out that the quantity of benzol to be extracted from coal by these processes (carbonizing it for that special purpose, and condensing the benzol from the gas by oily absorbents) is thirty times the amount of that yielded by coal in the ordinary process, namely, allowing most of the benzol to remain in the gas, and only recovering what is found in the tar. The benzol obtained by the new processes, however, is not so easily nitrifiable as that made from tar.

*Extraction of Benzol from Coke-oven Gases.*

The quantity of benzol present in coke-oven gases is not so great as that contained in illuminating-gas, but quite sufficient to make it worth while extracting it; Kraemer (*Glückauf*, 1897, p. 381) estimates it equal to half of that found in illuminating-gas. According to Haarmann (*loc. cit.*, p. 28), the Westphalian factories in the year 1900 obtained on the average 0.4 per cent. benzol and 0.09 per cent. toluol from the coal coked; the factories of the Laar district recovered on the average 0.9 to 1.0 per cent. benzol from the coke-oven gases. According to Brunck (communic. to Dr Köhler), the yield of benzol depends not merely upon the quality of the coal and the temperature of coking, but also upon the tightness of the oven-walls; in the various German coking-districts the yield ranges from 0.4 to 1.0 per cent. of 90 per cent. benzol and 0.15 to 0.3 per cent. of its homologues. In Westphalia the yield is from 0.75 to 1.45 per cent. of the coal. Comparing this with Bunte's statement that the Karlsruhe illuminating-gas contains 1.25 benzol on 100 coal charged into the retorts, the difference in the benzol contents of illuminating- and coke-oven gas cannot be very serious.

Whilst in the case of ordinary illuminating-gas it is a doubtful advantage to extract from it its most valuable light-giving constituent, benzene, and thus to greatly reduce its value, and while at the present time the carbonization of coal in such a way as to make the production of benzol the principal aim is utterly unremunerative, it seems a much more promising idea to submit the gases obtained *as a by-product in coke-making* to a similar treatment for extracting the benzol, instead of burning the latter as fuel for the coke-ovens, along with the

great bulk of those gases. It is evident that in this case the benzol may be considered as a clear profit; for the gases are always more than sufficient for heating the coke-ovens, even after abstracting the benzol. Although the great industry which has sprung up in that line does not apply to ordinary illuminating-gas, but to that of coke-oven gases, treated in the next section, we shall describe the apparatus used for that purpose in this place, since it is entirely on the same lines as that intended for taking the benzol out of retort-made illuminating-gas.

The pioneer in this field was Carvès (B. P. 15920, 1884), who applied the process to the gases produced in his own coke-ovens (*cf.* later on).<sup>1</sup> He employs as an absorbent for extracting the benzol from his waste gases the heavy portions of the oil obtained in the distillation of the tar procured from his own ovens. The gas is first made to pass through scrubbers consisting of upright cylinders, filled with pebbles or ganister, over which the oil is made to flow down. From the scrubbers the gas passes into one or more wash-boxes, the lower compartment of which is again charged with heavy oil, and communicates with an upper compartment by means of a great number of small tubes passing down from the partition and dipping into the oil, so that the gases entering above are caused, by pressure or by exhaust at the exit of the lower compartment, to pass down these tubes and to bubble up through the liquid. Several of these wash-boxes are employed in combination, and are so arranged that the oil flows downward from the first to the second, and so on to the last one, while the gases first enter the lowest and successively pass on to the highest wash-box, and thence to the ovens, to be burned. The oil coming from the lowest box is further made to feed the above-mentioned scrubber, so that the gases richest in light hydrocarbons come into contact with the oil which has already taken up most of the hydrocarbons from the preceding gas, and the almost exhausted gas is always brought into contact with fresh oil. In order to separate the benzol from the heavy oil, the mixture is heated in a still provided with an external steam-coil, or heated from without by a fire or by a

<sup>1</sup> A patent for the same idea has also been taken out by J. Coates (B. P. 11202, 1885).

coke-oven gas, to a point where the light oils are volatilized while the heavy oil is not affected. The escaping vapours are condensed in a worm in the usual manner; the heavy oil remaining behind is used over again in the wash-boxes and scrubbers, as described above.

The process of Carvès does not seem to have been carried out on a real working scale in his own country. This was done first by Brunck, in 1887 (*Stahl u. Eisen*, 1892, p. 186; 1894, No. 15; 1900, No. 13; 1910, Nos. 29, 30, 35, 37, 38, 49), at Dortmund, and by Hüssener at Gelsenkirchen.

Since that time a number of benzol-recovery plants have been erected in Germany on the lines laid down by Carvès. The coke-oven gas is first cooled down in the usual way, to condense most of the tar and part of the ammonia; the remainder of the ammonia is then removed by scrubbing with water, and the gases are then passed through similar scrubbers (*e.g.*, towers with many perforated shelves, the holes being luted by bell-covers), which are fed with heavy coal-tar oil.

Donath (*Fischer's Jahresber.*, 1894, p. 21) gives some details on the above subject, from which we quote the following notes. The gas is forced through the absorbing-columns by means of a blowing-engine, but first passes a collector and a cooler, to equalize the current and to remove the heat generated in compression. The columns are 7 ft. wide and 10 ft. high, and resemble those employed in ammonia-soda works, the gas entering from below. The absorbing oil takes up at most 10 per cent. of its weight of benzol, sometimes only 6 or 7 per cent. All of this has to be heated to 200° C., in order to distil off the benzol. The coolers, connected with the stills, serve at the same time for a previous heating of the benzol-oil. The absorbing-oils can be used twenty times over again before they become too thick by the accumulation of naphthalene and tar, and must be removed. This loss amounts to about 5 per cent. per annum. The cost of plant for treating the gas from 300 tons of coke per day is £4300; the expense of working, inclusive of interest and amortization, is about £4350 per annum. The yield of benzol varies from 0.3 to 0.7 per cent. of the coal carbonized.

*Process of Hirzel.*—We owe the following details and diagrams to Dr H. Hirzel, Leipzig-Platwitz. Fig. 6 shows a

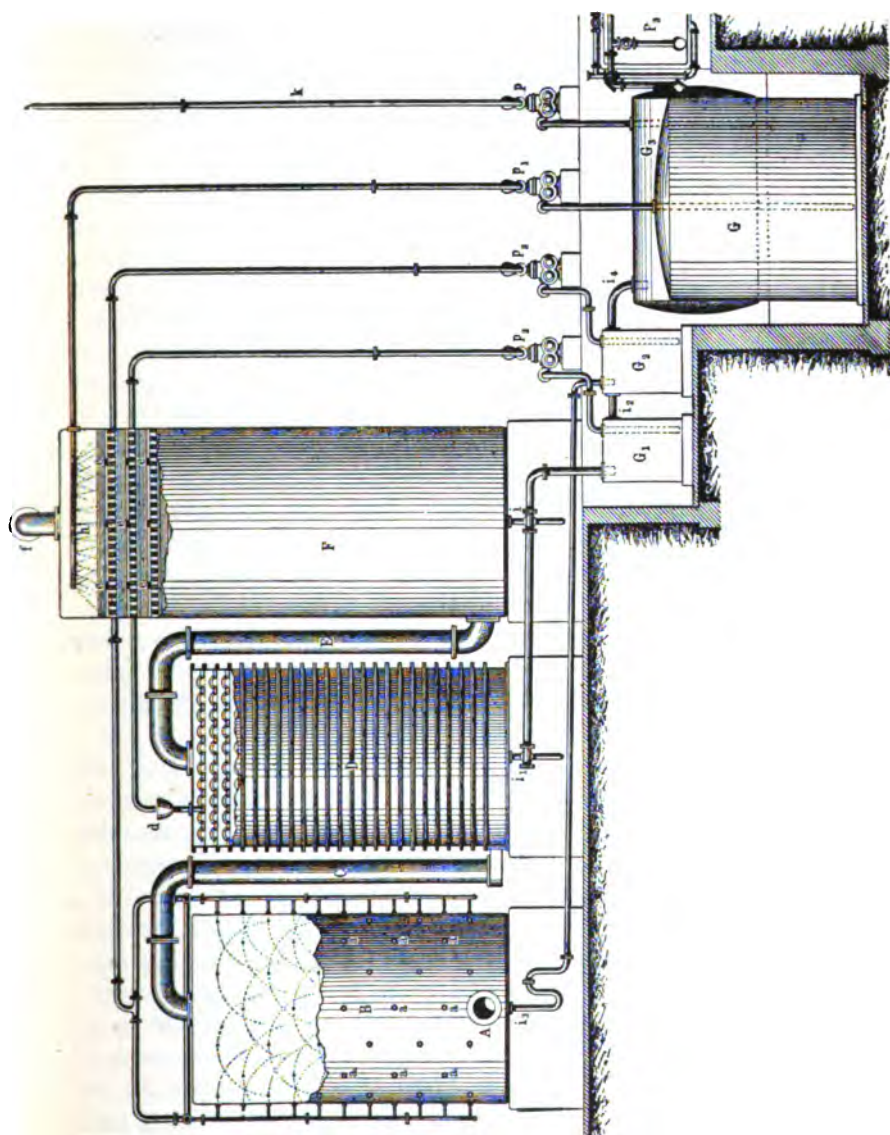


FIG. 6.



complete benzol-absorbing or "oil-washing" plant, according to Hirzel's German patent No. 99379, for treating from 3,500,000 to 5,200,000 cubic feet of coke-oven gas per 24 hours. There are three oil-washers of different construction, 8 to 10 feet wide and 16 to 23 feet high. A set of pipes, 18 to 20 inches wide, conveys the gas from below, at A, first into a Hirzel's tuyere-washer (Ger P. 96228), into which the oil is forced through 200 up to 400 jets (*a*) in such manner that a spray is formed, filling the whole of the space, which quickly and completely removed the oil from the gas coming from the washer B. From here the gas travels through pipe C into a "bell-washer," D, and passes through this also from the bottom upwards, being constantly brought into contact with the oil by means of the bells or caps dipping into the oil. The latter enters at the top at *d*, and descends from compartment to compartment. These washers are now made with 24 or more compartments, containing 3000 or 4000 bells. They act very well, but are more complicated and expensive than the tuyere-washers. Lastly, the gas enters through E into the "shelf-washer" F, and leaves this at the top at *f*. This washer contains a number, say 28, of superposed wooden latticework or wirework shelves, on which the oil runs from the sprinkler *h*, passing through the interstices of the lattice shelves.

Whilst the current of the gas travels from A to B, D, F, and comes out at *f*, the washing-oil travels in the opposite direction. It is pumped from the store-tank G by pump  $p_1$ , first into the last washer F, where it meets almost debenzolized gas and takes the last benzol out of it; it flows through *i* into tank  $G_1$ , from this through pump  $p_2$  into the bell-washer D, and through  $i_1$  back into  $G_1$ . The overflow from  $G_1$  leads through  $i_2$  into tank  $G_2$ ; from here pump  $p_3$  forces the oil into the tuyere-washer B, where it meets with fresh gas and is now run back through  $i_3$  into  $G_2$ . The overflow of this tank leads through  $i_4$  into the collecting tank  $G_3$ , from which the now enriched oil is pumped by pump  $p$  through pipe *k* into the stills (see below).

Some manufacturers employ two different kinds of washing-oil, but Hirzel prefers using only one quality, which serves for taking 98 per cent. of all benzol out of the gas. The oil must

be neither too thin (as it will then not remain long enough in contact with the gas) nor too thick (as it will then froth and solidify in the cold). The best oil yields:—

Distilling off up to 240° C.,			6 per cent.	
"	"	250	further	13
"	"	270	"	27
"	"	280	"	12
"	"	300	"	25
"	"	310	"	6
"	"	320	"	5
Solid residue	.	.	.	6
				<u>100</u>

Care should be taken that very little distils over 300° C.

It is also very important to employ the oil at the proper temperature. Already at 25° C. it loses some of its absorbing-capacity, and at 40° most of it. The best temperature is from 15° to 20°; an artificial cooling to 10° or below does not offer an advantage corresponding to the trouble.

From  $G_3$  the oil is continuously pumped by  $p$  through  $k$  into the elevated store-tank H (Fig. 7), and is from here continuously fed into one or more Hirzel's stills, K. First the oil, conveyed through pipe  $k$ , passes the heater J  $J_1$  from the bottom upwards. The lower part, J, is heated by the vapours coming from column K; the top part,  $J_1$ , is heated by direct steam. The warm oil leaves the heater  $k_1$ , and through  $k_2$  enters the column K near the top. This column is provided with steam-heating coils, placed in each chamber, covered by the oil, and heating this up to 110° or 115°. This is necessary to enable a slow current of dry steam to drive out the benzol. At the top, through  $k_3$ , steam and benzol vapours escape, pass through the lower part of the heater J, and from here enter the condenser M. From here the water and the crude benzol run into the separator N, with its vapour-pipe  $m$ ; and from this the water runs off at  $n$ , the crude benzol (visibly) through  $n_1$  and  $n_2$  into tank O.

Such a column of 3 feet 3 inches diameter distils in 24 hours 60 cubic metres (about 2000 cubic feet) of saturated washing-oil at a pressure of 4 or 5, or even 3, atmospheres. If the temperature in the columns is properly regulated, by the aid of thermometer  $t$ , to stand at 115° C., the crude benzol collecting in O tests regularly 50 per cent., and is very little coloured. At



130° the vapours already contain part of the washing-oil and at 150° to 160° this can be entirely brought over (see below).

The hot washing-oil, now free from benzol, leaves the column through *o*, runs into the cooler P, then through other coolers P<sub>1</sub>, P<sub>2</sub>, or more, and at last into tank G (shown also in Fig. 6). It is therefore in constant circulation.

The 50 per cent. crude benzol from O is usually rectified for 90 per cent. benzol. It is for this purpose run into the steam-still Q, with a column-top, R, a dephlegmator, R<sub>1</sub>, and a condenser, S. From the latter we obtain "first runnings," then 90 per cent. benzol and "last runnings" (toluol, etc.). These flow into the separator T, with vapour-pipe *s*; the water alone runs off through *v*, the distillates (visibly) at *v*<sub>1</sub>; the three-way cock *v*<sub>1</sub> directs them into either of the receivers, V, V<sub>1</sub>, or V<sub>2</sub>. The 90 per cent. benzol thus obtained is perfectly colourless, limpid, and easily purified in the usual manner by washing with sulphuric acid and caustic-soda solution. The residue remaining in Q is collected by itself or mixed with the washing-oil.

If the temperature of 115° in the still is not exceeded, the washing-oil suffers no decomposition and very little of it is lost. It might be used over and over again for ever, if the coke-oven gases coming from the condensers were free from tarry matters. But the condensers usually employed do not purify them sufficiently from naphthalene and tarry matters, which collect in the washing-oil and gradually diminish its absorbing-power. Spent oil sometimes contains 50 per cent. of naphthalene and pitch. Such oil must be regenerated, which can be done by distilling it in ordinary tar-stills; but this produces a washing-oil containing too much naphthalene and constituents boiling over 300°. It is much better to regenerate the spent washing-oil in a heatable Hirzel-column at 150° to 160° C., in which case the distillate consists essentially of oils boiling below 300° C., and, after separating the naphthalene by cooling, forms a most excellent absorbing-oil. The residue from the column is good soft pitch.

The above-described process had been carried out in the year 1900 in twelve large plants. Its advantages are: treating very large quantities of coke-oven gas in a limited space, distilling the washing-oil *continuously*, and obtaining at

once 50 per cent., by a second distillation colourless 90-per-cent. benzol. The consumption of steam and cooling-water, owing to the low temperature, is comparatively small. The work is automatic, and one man can superintend the whole plant.

*Other processes for the recovery of Benzol from Gases.*—Marks (B. P. of the Compagnie pour la Fabrication des Compteurs et Matériels d'Usines, No. 10577, 1897) employs for this purpose revolving drums, through which both the absorbing liquid and the gases travel in a circuitous way.

For washing out benzol from coal-gas or coke-oven gas, Heuss recommends a mixture of equal proportions of creosote oil, containing not above 2 per cent. of naphthalene, and anthracene oil, which yields no notable secretion of anthracene when cooled down to  $-4^{\circ}$  (private communication).

Heinzerling (B. P. 12390, 1892) condenses benzol from the gases from shale and coke by means of *cold*, either directly or after removing the tar and ammonia. They are then compressed and cooled down to  $+5^{\circ}$  or  $10^{\circ}$  C., or passed direct into a solution of sodium or calcium chloride, kept at temperatures of  $-10^{\circ}$  down to  $-45^{\circ}$ . Here most of the benzene is separated as a kind of grease on the surface. The escaping gases are forced to yield the liquid drops carried along by passing them through sieves, and then enter into an expansion cylinder, where they are brought down to a plus-pressure of  $\frac{1}{2}$  or  $\frac{1}{4}$  atmosphere, utilizing the mechanical force thus generated to compress a further portion of fresh gas. The gas issuing from this cylinder is again deprived of liquid particles, and is used for a preliminary cooling of the above-mentioned saline solutions. The latter may be dispensed with by simply allowing the compressed and cooled gas to expand, which causes the benzol to separate out in consequence of the fall of temperature, and admits of cooling fresh compressed gas by the same means. This process was practically carried out at a Silesian works, for recovering the benzol from 40,000 cubic metres gas per day. About 145 tons of crude benzol were actually obtained at a cost of 13s. per 100 kg. crude benzol, apart from interest and amortization. Owing to this, under most conditions excessive, cost and other circumstances, the process was stopped.

The Gewerkschaft König Ludwig (Ger. P. 136780) scrub the gases as usual with heavy coal-oil on the counter-current principle, and expel the volatile parts absorbed by means of steam, overheated to 300°, in which case all the naphthalene is also expelled, so that the absorbing-oil, after cooling, can serve over and over again.

Sorel (B. P. 242, 1900; *J. Soc. Chem. Ind.*, 1900, p. 337) distils the oil containing benzol by means of steam in a continuous-distillation column so constructed as to admit of separating the vapours into as many products as there are condensers employed, and thus varying the quantity and composition of each fraction at will. This he effects by partial cooling down to the temperatures of ebullition of the mixtures of steam and the single hydrocarbons concerned. At 93° C. nearly the whole of the xylene will escape condensation, but at 82° C. almost all the xylene will be condensed, without much toluene; at 72° a product very rich in toluene and heptylene will be condensed; below 65° almost all the benzene, without sensibly affecting hexylene or carbon disulphide.

Wilhelm (*Z. für chem. Apparatenkunde*, 1907, pp. 1 and 33) discusses the various processes for absorbing the benzol from the coke-oven gas. The scrubbers, containing superposed sieves for converting the absorbing oils into drops, are less expensive to work than the column apparatus, as these require a pretty strong pressure to force the gas through the liquid. The absorbing-oil, which takes up about 2 per cent. benzol, is first employed for cooling hot tar-oils, and is thus heated up to 80° C.; after this it is treated with open steam in distilling-columns to expel the benzol. Before using it again for absorbing benzol, it is cooled down to 18° or 20° C. After having been in use for some time, its absorbing powers are reduced; it is then run into the tar-pit, and fresh tar-oil is introduced into the process. The crude benzol is rectified and purified in the usual manner (as described in this volume, Chapter XI.), and is sent out as pure benzene, toluene, xylene, and solvent naphtha.

At the Bulmke works of the Aktien-Gesellschaft für Kohlendestillation A. Hüssener, the recovery of benzol from the gases has been greatly improved by cooling the absorbing-oils by means of a Linde cold-producing machine down to about

0° C. By this means up to 95.4 per cent. of the benzol contained in the gases has been recovered, the average being 93 per cent.

Kunow (Ger. P. 143307), very much like Hirzel, introduces the absorbing-oil into the gas by means of atomizing it, and employing a steam jet at the same time.

According to Schreiber (*Entwicklung der Kokereiindustrie Niederschlesiens*, 1911, p. 35), in Lower Silesia benzol-washers are employed, similar to ammonia-washers, according to a patent by Zschokke, 50 to 59 ft. high and 10 ft. diameter. For each 1000 cubic metres (= 35316 cub. ft.) of gas the washing-surface should not be less than 120 superficial metres (= 1237 sq. ft.) of washing surface. Each 1000 sq. metres washing-surface should occupy 15 cub. metres.

The above-mentioned process of Franz Brunck (p. 72) for the benzol recovery from coke-oven gases was first introduced at the Kaiserstuhl pit in 1887, and during the following years a series of such plants was erected at Westphalian and Silesian coke-works. The largest of these, for 300 coke-ovens, at the Julenhütte in Upper Silesia, was improved in 1894 by the introduction of continuously acting oil-washers, employing to begin with tar-oils boiling at 160° to 200°, and, following these, heavy oils boiling at 200° to 300°. This improved plant is described and illustrated in Lunge-Köhler's *Industrie des Steinkohlenteers und Ammoniaks*, 1912, pp. 145 to 148, where we also find on pp. 148 to 150 the description and illustration of the newest plant of the firm Dr C. Otto & Co., and on pp. 155 to 163 that of the firm Carl Still, of Recklinghausen (Westphalia).

Descriptions of plants for the recovery of benzol from coke-oven gases are given by Groeck (Collin's ovens, *Z. Verein. deutsch. Ingen.*, 1915, p. 116); Gossler (Ger. P. 282488; *Z. angew. Chem.*, 1915, ii., p. 269); Pietrusky (*Chem. Ind.*, 1915, p. 200; plants of the Cambria Steel Co., of the coke-works at Woodward, Alta., of the Tennessee Coal and Iron Co., of the United States Steel Corporation, etc., etc.).

Barnick (*Chem. Apparatur*, 1915, pp. 1 et seq.) describes with illustrations the apparatus employed at German coke-works for obtaining the benzol from the gases, as well as the plant for rectifying the crude benzol.

Diamond (*J. Gas Lighting*, 1915, p. 267; *J. Soc. Chem. Ind.*, 1915, p. 539) states that to recover the maximum quantity of benzol from coal-gas, the washing oil should have a sp. gr. between 1.04 and 1.06. Coal-tar creosote absorbs five times as much benzol as filtered anthracene oil. The amount of water in the washing oil should not exceed 1 per cent.; the presence of 2.5 per cent. in creosote oil reduces its efficiency by over 35 per cent., 7.5 per cent. by 45 per cent., and 10 per cent. by 73 per cent. By reducing the temperature of the gas below 15°, and that of the washing oil to 0°, absorption is increased by 20 per cent., but the cost of the cooling is prohibitive. The extraction of 2.1 gall. of benzol from gas per ton of coal results in a decrease of 4.5 per cent. in the calorific value of the gas; removal of 2.5 gall. produces a decrease of 7 per cent., and of 3 gall. a decrease of 8 per cent.

*Toluene* is also recovered from coal-gas. According to *J. Gas Lighting*, 30th March 1915; *J. Soc. Chem. Ind.*, 1915, p. 416, the Gas-Light and Coke Co. has been treating daily 15 million cub. ft. of gas at Beckton for the recovery of toluene, and this quantity will be increased shortly to 20 million cub. ft. Research and large scale experiments have led to finding out the most suitable wash-oil and the quantity of oil required to extract a maximum quantity of toluol without materially reducing the illuminating power or calorific value of the gas. By using a limited amount of oil in the washers, very little benzene is extracted from the gas, and a crude spirit is obtained, rich in toluene, xylene, naphthalene, etc. By this means, only a small quantity of benzol has to be returned to the gas, and the plant for dealing with the saturated oil is comparatively small. Rotary and centrifugal washers are used for the absorption of the toluol by the wash-oil.

The method of working is as follows:—The cooled debenzolized oil is pumped from the cold-oil store-tank at a constant rate through the washer, where it meets an opposing stream of gas. From the washer, the oil, now containing the toluene, etc., runs into a store-tank, from which it is pumped through the counter-current heat-economisers to the stills, in which the wash-oil and the light spirit are separated by means of steam. This method of separation is not unduly expensive in steam, provided the wash-oil in the extraction



washer is not used excessively. To secure further economy, it is proposed to make a trial of a direct-heated coil, an expansion chamber being worked on the outlet. The hot wash-oil from the still flows to a collecting-tank, from which it is pumped through the heat-exchangers, and onwards through water-coolers, after which it flows to the store-tank, from which the extraction washer is fed. The light spirit-vapours, after leaving the still, are conducted through a condenser, the condensed mixture of benzene and toluene flowing to a collecting tank after the separation of the condensed water. The mixture of spirit is afterwards rectified in a fractionating boiler, where the lighter spirit is separated from the toluene, xylene, etc., before this heavier boiling portion is sent to the products work for rectification—a yield of about one-third gallon of pure toluene per ton of coal carbonized being obtained.

Davidson (*J. Ind. Eng. Chem.*, 1915, p. 438) states that coal-gas contains from twenty to forty times as much toluene as the tar produced at the same time, and that from 10,000 cub. ft. of gas 2 lb. of pure toluene can be obtained.

Statistics on the recovery of benzol from coke-oven gases are given later on, in connection with the treatment of these gases for tar and ammonia.

#### *Recovering the Benzol from Coal-gas as Nitrobenzol.*

Attempts have been made to extract the benzol from coal-gas in a different manner, namely, by *passing the gas through nitric acid*, or a mixture of nitric and sulphuric acids. This was patented by Leigh as early as 1863, but nothing came of it. The process was once more taken up by J. A. Kendal (U.S. P. 252473, 1882), who first passed the gas through strong sulphuric acid, in order to extract from it those hydrocarbons (belonging to the "unsaturated" fatty series) which are an impediment to the ready nitrification of the benzene, which process was effected by a second passage through a mixture of nitric and sulphuric acids. It is not possible to avoid the formation of dinitrobenzene; and Kendal, from the first, set out with the intention of producing this compound as the principal product. Evidently the process did not pay; and it

was therefore modified in such a manner as rendered the previous removal of the unsaturated fatty hydrocarbons unnecessary (B. P. 1541, 1882; Ger. P. 24318). The coal-gas is passed through a superheater consisting of metal tubes partly filled with coke or charcoal and kept at a red heat. The flow of gas is regulated by a valve or meter to the point at which most benzol is produced for a given weight of gas. This is ascertained by passing a trial quantity through a vessel containing a mixture of 1 part of strong nitric acid and 5 parts of strong sulphuric acid up to the point where the change of colour shows the mixture to be saturated with benzol. The dinitrobenzene formed is precipitated by water, dried, and weighed. This test is repeated till the best proportions for the given case are found. As an instance, good results were obtained by passing 8000 cubic feet of gas per hour through nine cast-iron pipes, 8 inches wide, and each exposed to the heat for a length of 10 feet. The superheating process reduces the illuminating-value of the gas, but it is asserted to increase the quality of benzol by from 5 to 40 per cent., and to make the gas fit for directly producing nitrobenzene or dinitrobenzene without a previous washing with strong sulphuric acid.

Kendal's process has been carried out on a manufacturing scale by Messrs Sadler & Co., of Middlesborough, who exhibited the products obtained by it at the Inventions Exhibition in London, 1885 (*J. Soc. Chem. Ind.*, 1885, p. 475). It evidently has the great drawback that most of the benzene is obtained as dinitrobenzene—a compound which is only employed to a limited extent in the manufacture of aniline colours. This process seems to have been abandoned again, after yielding somewhat considerable quantities of dinitrobenzene and dinitrotoluene.

*Composition of Benzol obtained from Coal-gas.*

Lunge and von Kéler (*Z. angew. Chem.*, 1894, p. 637) have analyzed two crude benzols from coke-ovens, one of which had been obtained by absorption, the other by the Heinzerling process (p. 78), with the following results:—

I. *Benzol made by absorption.*—Clear, yellow liquid of un-

pleasant, tarry smell; spec. grav. at  $16^{\circ} = 0.875$ . Commences to distil at  $18^{\circ} \text{C.}$ ; it yields the following fractions:—

			Per cent.				Per cent.
From $18^{\circ}$ to $28^{\circ}$	.	.	0.01	From $81^{\circ}$ to $91^{\circ}$	.	.	20.44
" 28 " 40	.	.	0.26	" 91 " 100	.	.	4.37
" 40 " 50	.	.	0.15	" 100 " 111	.	.	8.96
" 50 " 60	.	.	0.50	" 111 " 140	.	.	2.27
" 60 " 70	.	.	1.62	" 140 " 150	.	.	0.78
" 70 " 81	.	.	58.92	Residue	.	.	0.62

Loss, 1.5 per cent.

II. *Benzol made by compression and cooling.*—Dark liquid, similar to "light-oil" from coal-tar; spec. grav. at  $16^{\circ} = 0.893$ . Begins to boil at  $30^{\circ}$ , and yields:—

			Per cent.				Per cent.
From $30^{\circ}$ to $50^{\circ}$	.	.	0.01	From $120^{\circ}$ to $140^{\circ}$	.	.	4.20
" 50 " 60	.	.	0.07	" 140 " 150	.	.	6.25
" 60 " 80	.	.	26.075	" 150 " 180	.	.	2.67
" 80 " 90	.	.	24.61	" 180 " 205	.	.	3.91
" 90 " 100	.	.	12.52	" 205 " 250	.	.	4.35
" 100 " 110	.	.	5.10	" 250 " 320	.	.	0.45
" 110 " 120	.	.	5.66	Residue (pitch)	.	.	1.50

Loss, 1.90 per cent.

The ultimate constituents of these distillates were separated as far as practicable by fractional distillations and by a number of chemical operations, described in the original; the final results are shown in the following table:—

Constituents.	Absorption- benzol.	Compression- benzol.
	Per cent.	Per cent.
Benzene . . . . .	85.10	67.03
Toluene . . . . .	11.63	15.61
Xylenes . . . . .	1.54	2.18
Higher homologues . . . . .	0.09	6.41
Naphthalene . . . . .	...	3.99
Higher-boiling aromatic hydrocarbons . . . . .	...	1.42
Non-saturated fatty hydrocarbons . . . . .	0.41	0.06
Thiophens . . . . .	0.46	0.71
Phenols . . . . .	0.08	0.11
Tar-bases . . . . .	0.08	0.28
Carbon disulphide . . . . .	0.01	...
Methyl-isocyanide . . . . .	0.0024	...
Mercaptans . . . . .	0.00018	...
Residue . . . . .	0.62	1.50

The difference between these two descriptions of benzol is undoubtedly caused by the fact that the absorption-benzol has left its high-boiling constituents in the absorbing-oil on redistillation.

According to Schreiber (*Koksindustrie Niederschlesiens*, 1911, p. 45), in Lower Silesia the light oil distilling from the benzol-washers of coke-ovens yielded 55 per cent. benzol (boiling-point up to  $100^{\circ}$ ), 17 per cent. toluol (boiling-point  $100^{\circ}$  to  $120^{\circ}$ ), 9 per cent. xylol ( $120^{\circ}$  to  $150^{\circ}$ ), 6 per cent. solvent naphtha ( $150^{\circ}$  to  $180^{\circ}$ ), and 15 per cent. residue.

*Estimation of Benzene and its Congeners in Coal-gas.*

Hempel and Dennis (*J. Gasbeleucht.*, 1891, p. 414) employed strong alcohol for absorbing the benzol contained in coal-gas. Dennis and O'Neill (*J. Amer. Chem. Soc.*, 1903, p. 503) found this unsatisfactory; they shake the gas during three minutes with an ammoniacal solution of nickel (16 g. nickel nitrate dissolved in 100 c.c. water + 2 c.c. concentrated nitric acid, and poured into 100 c.c. concentrated liquor ammoniæ). Before measuring the contraction, the ammonia vapours must be removed from the gas. To this Morton (*ead. loco*, 1906, xxviii, p. 1728) objects that that reagent has only the dissolving power of water or dilute ammonia for benzol; he, on his part, considers as the only proper method for estimating benzol in coal-gas, the absorption by sulphuric acid of specific gravity 1.84, a correction being made for the absorption of non-saturated aliphatic hydrocarbons. To this Dennis and M'Carthy reply in the same journal, 1908, xxx., p. 233. They now employ an ammoniacal solution of nickel cyanide which quantitatively absorbs the benzene from air or coal-gas. The reagent is prepared by adding a solution of 25 g. of potassium cyanide in 40 c.c. water, to a solution of 50 g. of nickel sulphate crystals in 75 c.c. water, then adding 125 c.c. ammoniacal liquor (sp. gr. 0.91), shaking and cooling down to  $0^{\circ}$  C., in order to precipitate the potassium sulphate. Pour off the clear liquid and add a solution of 18 g. citric acid crystals in 10 c.c. water; allow to stand at  $0^{\circ}$  C. for ten minutes, decant the liquid and transfer it to a Hempel pipette, the upper bulb of which is filled with broken glass. The gas to be analysed is passed in and out

several times, and is then transferred to a similar pipette containing sulphuric acid, to remove ammonia. The nickel cyanide solution prepared as above does not absorb measurable amounts of ethylene or other constituents of ordinary coal-gas, except those which can be absorbed by potassium hydroxide solution. The authors find that the method suggested by Morton, as above quoted, does not yield constant results. The strong sulphuric acid absorbs both ethylene and benzene, and presents difficulties in manipulation, by frothing to such an extent as to make the accurate reading of the gas volumes well-nigh impossible.

Harbeck and Lunge (*Z. anorg. Chem.*, 1898, xvi., 41) pass the gas through about 110 c.c. of a mixture of equal parts of concentrated pure sulphuric and nitric acid, contained in a 15-bulb tube which retains the benzene as dinitrobenzene. The latter is separated by diluting and neutralizing the acid mixture; it is then dried and weighed. Pfeiffer (*J. Gasbeleucht.*, 1899, p. 697) employs this method in a somewhat simplified form. The same author later on (*Z. angew. Chem.*, 1905, 1156) shortens the process by titrating (instead of weighing) the dinitrobenzene; he reduces it by stannous chloride and titrates the excess of this with decinormal iodine and starch solution.

Haber and Oechelhäuser (*Ber.*, xxix., p. 2700), in a first operation, estimate the benzene and ethylene together in the usual absorptiometric way, and then ethylene by itself, by means of bromine vapour which combines with the ethylene, but not with the benzene vapour; so that the latter is found by difference. In 1900 Haber once more draws attention to this process and justifies its accuracy. He proceeds as follows. Determine the contents of a Bunte burette below the lowest division to the tap by weighing. Introduce about 90 c.c. of the gas to be tested and read off. Draw off all the water by aspiration exactly down to the tap, allowing a few minutes for the water adhering to the sides to collect, and drawing off this last drop as well. Pour about 35 c.c. bromine water from a stock bottle into a cup; allow 10 to 15 c.c. of this to enter into the burette; observe the volume in the burette, and allow a few drops of water to enter from below in order to force the bromine contained in the capillary below the tap into the burette. Incline and turn the burette so as to fill it with bromine vapour whose

brown colour must prevail up to the end. After two or three minutes allow a strong solution of potassium iodide to enter, shake well, empty the contents of the burette into a beaker, rinse it with water, and titrate the free iodine by thiosulphate solution, noting the temperature and atmospheric pressure. Before and after this operation estimate the percentage of the bromine water in the stock bottle by titrating 10 c.c. with KJ and thiosulphate; the average of those two tests, which ought to differ very little, is employed for calculating the result. One litre of decinormal thiosulphate = 1.121 litre of dry ethylene at 0° and 760 mm. The bromine water employed should be decinormal or even weaker.

Pfeiffer (*Chem. Zeit.*, 1904, p. 884) passes the gas through strong nitric acid, thus producing dinitrobenzene, which is either weighed or reduced by stannous chloride and titrated with iodine solution and starch.

Misteli (*Z. angew. Chem.*, 1905, p. 393) discusses various methods for the same purpose; so does Stavorinus (*J. Gasbeleucht.*, 1905, p. 272). He specially recommends the methods of Dennis and O'Neill, who apply ammoniacal nickel nitrate (*Chemische Zeitschrift*, ii., 229).

Müller (*J. Gasbeleucht.*, 1898, p. 221) absorbs the benzol in cooled paraffin oil. Special apparatus for this purpose is described by Nowicki (*ibid.*, 1905, p. 292); Jenkins (*Stahl u. Eisen*, 1912, p. 1129); Krieger (*J. Gasbeleucht.*, 1915, p. 62). Other methods have been described by Reineke (*Ger. P.* 285920) and by Burrell and Robertson (*J. Ind. Eng. Chem.*, 1915, p. 669).

#### *B. Tar (and Ammonia) obtained as By-products in Coke-making.*

We have seen above (p. 17) that more than a hundred years ago a somewhat successful attempt was made (by Stauf) to recover the tar formed in the coking of coal. It is not surprising that nothing further should have come of this; for in the first instance it must have been soon perceived that there was no profitable outlet for coal-tar at that time, and moreover, it is very likely that the quality of the coke suffered under this kind of treatment.

For a long while after the extraction of tar and ammonia had been recognized as a very valuable accessory of gas-making it was firmly believed that only inferior coke could be produced

in this way, similar to what is obtained in retorts at the gas-works, and that the coke required for metallurgical purposes, more especially for blast-furnaces, could only be obtained in beehive-ovens or similar apparatus, untrammelled by contrivances for dealing with the gases or the condensable products contained therein. It had certainly been proved for some time past that at least the combustible gases escaping from the mouths of coke-ovens could be utilized in a more profitable manner than for illuminating the surrounding pit-heaps at night; and the improved coke-ovens constructed by Appolt, Smet, Coppée, and others had been for thirty years in general use in Germany, Belgium, and France, before in Great Britain anything seemed to shake the belief of iron-smelters in the infallibility of the beehive-oven. But even on the Continent it was thought that, although the gases might be advantageously used for supplying the heat necessary for the destructive distillation of the coal, any attempt at condensing tar and ammonia must necessarily be fatal to the quality of the coke. This belief has long since been proved to be altogether unfounded.

Certainly, as we shall see below, the tar formed in the open beehive-ovens, which in Great Britain are the type almost universally adopted, is a substance very different indeed from gas-retort tar, and it is questionable whether its collection will always pay for the expense of it; but it is altogether different with the tar from the "close" coke-ovens long since introduced on the Continent, which tar is practically equal to normal gas-tar. This difference in the quality of the tar is caused by two circumstances, viz. :—first, that in the beehive-ovens and all similar ovens air is admitted into the coking-chamber, and, secondly, that the temperature in these ovens is very much below that obtained in the close coke-ovens and the gas-retorts.

The process of obtaining tar and ammonia as by-products in coke-making (not reckoning the abortive attempt of Stauf) originated in France, and remained stationary for a remarkably long time until, all at once, about the year 1881, new interest was awakened in the subject, and it was taken up with almost feverish activity, more especially in Germany, but also in Great Britain, much less so in its original home in France. It seems that the first apparatus of this kind was that constructed by

Knab in 1856,<sup>1</sup> of St Denis, near Paris, at Commentry; but the condensation of tar and ammonia in these ovens was only later on introduced by Hauptart and Carvès. The principal advantage of Knab's ovens was the increase of the yield of coke to 62.55 per cent., instead of the 54 or 56 per cent. previously obtained.

Knab's (or rather, Hauptart and Carvès') priority has been contested by a note in *Dingl. polyt. J.* (vol. ccl., p. 524), according to which there were fifty Pauwels-Dubochet coke-ovens at work near Saarbrücken as early as 1854; but Gurlt (in a letter to Mr Watson Smith, *J. Soc. Chem. Ind.*, 1884, p. 603) points out that no tar was then produced from the Dubochet ovens at Saarbrücken, all the gases and products of distillation being burned around the coking-chamber to heat it. From the description of the Pauwels-Dubochet ovens, which Oechelhäuser examined in 1860 during a visit to the La-Villette works of the Paris Gas Company,<sup>2</sup> it would appear that they had then been for some time in use for the production of excellent metallurgical coke, along with rather poor illuminating-gas, which was mixed with the richer gas made in ordinary gas-retorts. The temperature in those ovens was much lower than in the Knab ovens. Tar and ammonia must necessarily have been condensed, since the gas was required for illuminating purposes; in fact, E. A. Behrens, who subsequently describes the same plant,<sup>3</sup> mentions that the yield of tar was 4.67 per cent., and that it was much lighter than retort-tar, and poorer in naphthalene and phenols. [The specific gravity (1.2) given for that tar is probably erroneous.] The Pauwels-Dubochet ovens seem to have been introduced merely on account of the higher value of the coke (at that time 35 fr. per ton, against 20 fr. for retort-coke), and appear to have been abandoned at La-Villette for some time past.

About the same time (1861) patents were taken out by Jones and by Blackwell for obtaining, by simple contrivances, tar and weak ammoniacal liquor when coking coal in pile. As

<sup>1</sup> Described in Armengaud's *Génie Industriel*, Aug. 1859, p. 71, and in *Dingl. polyt. J.*, vol. cliv., p. 97. Compare, with reference to the following historical notes, apart from the first edition of this work, also Gurlt, *Die Bereitung der Steinkohlenbriquettes*, p. 28; Hüssener in *Stahl u. Eisen*, 1883, p. 397; and W. Smith, *J. Soc. Chem. Ind.*, 1884, p. 603.

<sup>2</sup> *Dingl. polyt. J.*, vol. clx., p. 394; Wagner's *Jahresber.*, 1861, p. 674.

<sup>3</sup> *J. prakt. Chem.*, vol. ccvi., p. 277.



might have been anticipated, these attempts were not crowned with any success. Jones's plan has been described by Watson Smith.<sup>1</sup>

Knab's original furnaces only possessed bottom flues beneath their beds. A considerable improvement was effected by Carvès, under whose management 88 Knab ovens were erected at St Etienne, which, however, were abolished later on. Carvès, at Commentry, first introduced the heating of the ovens by side flues in addition to the bottom flues. A description of those furnaces, as they were working in 1862, has been given by Gaultier de Claubry.<sup>2</sup> The gases and vapours escaping from the closed coke-ovens were passed into a hydraulic main cooled by air, where tar and ammonia condensed, while the gases were continually drawn off by exhausters, and employed for heating the coke-ovens, by issuing from an annular burner along with air admitted into its inner space. In order to collect the condensable products more completely, the gas was first passed through coke-scrubbers fed with water, and then through a set of 500 upright lead pipes of  $\frac{3}{8}$ -inch width, externally cooled by water.

From 100 parts of coal there was obtained:—

	Per cent.
Coarse coke . . . . .	70.00
"Pea coke" . . . . .	1.50
Coke rubbish (waste) . . . . .	2.50
Graphite . . . . .	0.50
Tar . . . . .	4.00
Ammoniacal liquor . . . . .	9.00
Gas . . . . .	10.58
Loss . . . . .	1.92
	<hr/> 100.00

The Knab-Carvès ovens were gradually introduced into other places. In the years 1866 to 1873, 53 such ovens were erected at Bessèges, and 100 ovens at Terre-Noire, near St Etienne, 1879.

The Bessèges coke-ovens have been minutely described by Dr Angus Smith,<sup>3</sup> who, with very great foresight, warmly

<sup>1</sup> *J. Soc. Chem. Ind.*, 1884, p. 604.

<sup>2</sup> *Bulletin de la Société d'encouragement*, 1862, p. 581.

<sup>3</sup> *Fourteenth and Fifteenth Reports on the Alkali Acts*, for 1877 and 1878, pp. 49 *et seq.*

recommended this system at a time when hardly anybody in Great Britain had taken any notice of it.

Further attention was drawn to the Carvès ovens by H. Simon, in a paper read to the Iron and Steel Institute in May 1880, but without making an immediate impression.

The Carvès ovens, as they were working at Bessèges in 1880, have been accurately described and figured in the *Bulletin de la Société de l'Industrie Minérale*, vol. ix., p. 283.<sup>1</sup> After many trials they were made only 2 feet wide, to allow of the heat penetrating them thoroughly. Over a small fire-grate is placed the mouth of a pipe conducting the gases formed in coking, from which tar and ammonia have been abstracted, and here they are burned. The products formed in combustion pass underneath the hearth of the oven, then travel upwards to the top-most of the three flues built in the side-walls, and downwards through these flues into the main flue leading to the chimney. The volatile products escape through a pipe from the interior of the coking-chamber; they first pass through a number of horizontal pipes, cooled by a stream of water, and then through scrubbers, where they are freed from tar and ammonia previously to being introduced into the combustion-chamber.

The more recent modifications of the Carvès ovens will be described lower down.

Pernolet's coke-ovens<sup>2</sup> are very similar to Knab's. From Gurlt's description (*loc. cit.*) it would appear that they were kept at a greater heat than Knab's. The condensing-plant for tar and ammonia was added to them by Benut and Renant, and seems to have been very well constructed, but a very unfavourable account of the working of the ovens themselves is given by Stevenson.<sup>3</sup>

In 1873, H. Aitken, of Falkirk, conceived the idea of drawing off tar- and ammonia-vapours from beehive-ovens, which was further developed in 1879.<sup>4</sup>

In 1879, Ströhmer and Schultz (Ger. P. 8174) proposed drawing off the gases and vapours from coke-ovens by a sliding tube before they had time to be decomposed by the heat of the brickwork. Lest the quality of the coke should suffer by the

<sup>1</sup> Quoted through *Dingl. polyt. J.*, vol. ccl., p. 254.

<sup>2</sup> Armengaud's *Génie Industriel*, June 1870, p. 281; *Dingl. polyt. J.*, vol. cxcvii., p. 411.

<sup>3</sup> *J. Soc. Chem. Ind.*, 1883, p. 604.

<sup>4</sup> Watson Smith, *ibid.*, 1884, p. 604.

gases being drawn off too fast, the sliding tube was raised or lowered by an automatic pressure-regulator. This plan was tried at Plauen, near Dresden, but without success.

In 1880, H. C. Bull patented an oven somewhat similar to Aitken's.

About that time Ed. Fischer constructed an oven for obtaining tar and ammonia from bituminous shale, and more particularly from the browncoal breeze found in enormous quantities in Bohemia in the shape of pit-heaps. The process is said to have answered well, but only yielded an inferior coke, fit for heating domestic stoves.<sup>1</sup>

Up to the year 1881 none of the processes for obtaining tar and ammonia in coke-making had been found to be thoroughly successful, especially with respect to the quality of the coke, so that a prize offered in 1870 by the Berlin Society for the Advancement of Industry was allowed to lapse. The only exception to this rule, the Carvès oven, had not become sufficiently known outside a comparatively small circle. Whilst many different ovens were known which utilized the heat of the gases evolved, and indeed such ovens were very generally employed on the Continent, the further problem of recovering the tar and ammonia without in any way injuring the quality of the coke for blast-furnace purposes was tacitly or expressly regarded as insoluble.

In 1881, the coke-making public in England and Germany almost suddenly became aware that the long-standing success of the Carvès oven was a reality, and that these ovens could even be improved upon. In England H. Simon, of Manchester, assiduously laboured for the introduction of Carvès' process, improved by a recuperator. In Germany the pioneers in this line were Hüssener, Otto, and Brunck. In the year 1881 Hüssener, of Essen, erected at Gelsenkirchen 50 coke-ovens of the Carvès type, utilizing the experience gained at gas-works on the recovery of the by-products. He worked with ordinary gas-coal, and from 14 to 15 per cent. of the coke obtained was used for heating the ovens, as in the manufacture of coal-gas. In consequence of its deficiency in forming hard lumps, the other portion of the coke could not be used at blast-furnaces, and therefore Hüssener's first attempt was

<sup>1</sup> Hüssener, *Stahl u. Eisen*, 1883, p. 409.

not successful; but he obtained excellent results when using normal "Fettkohle" (bituminous coal), both as to the quality of coke and the by-products. He then built 50 coke-ovens, in which the better distribution of the gases and its combustion in the side-flues made it possible to dispense with coke as fuel, so that the ovens could be heated exclusively by their own gases and even left an excess of gas available for heating and lighting purposes. These ovens were fitted with horizontal flues.

Otto had since 1872 built Coppée coke-ovens with perpendicular side-flues and utilization of the coking-gases for heating them, with various improvements of his own. Ten of these he connected with arrangements for recovering the by-products, but with imperfect success. Continued experiments led his firm (Dr C. Otto & Co.) in the year 1881 to build ovens fitted with a Siemen's regenerative plant, which have become known as Hoffmann-Otto coke-ovens; twenty of these started working in 1884, at the Pluto pit, near Wanne. Up to 1895 this plant was considered the best of those working in Germany, after the regenerator had been confined to the air and the combustion of the gases had been removed from the oven bottom to the sides.

In 1887 Franz Brunck, of Dortmund, introduced the recovery of benzol from coke-oven gases (*supra*, pp. 70 *et seq.*), a step of extreme importance for all the industries connected with benzol, as well as for the German coke industry. His patents are enumerated in the list given below.

During a number of years that new industry had to struggle with the prejudice of iron-makers, who believed the coke made in the by-product recovery furnaces to be less valuable than that made in the old beehive-ovens. That prejudice was widely prevalent, especially in Great Britain, until quite recently. Outside of Germany up to 1900 only a very small number of such furnaces were erected. In Germany also the by-product recovery coke industry would not have taken such a rapid development as has been actually the case, if Otto had not most materially advanced it by offering to coal-miners to erect such plant free of cost, with the sole condition of handing over to him the by-products, tar, benzol, and ammonia, during a number of years.

In Germany, Silesia was the first mining district in which no more coke was made without recovering the by-products. A little slower was the progress made in the Ruhr and Saar districts, but whereas in the year 1900 only 30 per cent. of the German coke was made with recovery of by-products, that percentage has risen in 1909 to 82.

To be sure, the cost of plant for the new system is much higher than for the beehive-ovens, and much greater claims must be made upon the skill of the workmen and the management. In some cases there is also a difficulty in disposing of the by-products at remunerative prices. This explains why, even in Germany quite recently, coke-ovens have been built on the old plan, in cases where there was no prospect of getting a corresponding greater revenue from the much more considerable cost of plant of the new system.

In Great Britain (according to Bury, *J. Gas Lighting, etc.*, 1909, p. 82) in the year 1900, only 10 per cent. of all the coke was made with recovery of the by-products; in the year 1909 this proportions had risen to 18 per cent. In 1905 (*J. Soc. Chem. Ind.*, 1907, p. 1230), of a total number of 257 coke-works, only 51 worked with recovery of by-products. The number of ovens of the various systems in the years 1905 and 1906 was as follows:—

	1905.	1906.
Coke-ovens of the old beehive shape . . .	25,514	23,454
"    on the plan of Coppée . . .	2,233	2,308
"    "    Simon-Carvès . . .	726	808
"    "    Otto-Hilgenstock . . .	503	768
"    "    Semet-Solvay . . .	470	670
"    "    Koppers . . .	72	108
"    "    Simplex . . .	78	78
"    "    Bauer . . .	52	52
"    of other systems . . .	1,412	1,782

In the year 1906 there were, moreover, in course of erection, 320 Semet-Solvay and 15 Otto-Hilgenstock furnaces.

In the United States (according to *Iron Age* of July 24, 1902), there was produced in the year 1901 altogether 21,495,853 tons of coke, of which only 1,799,000 tons were made with recovery of by-products. The following table is taken for the years 1901 to 1906 from the United States *Geological Survey*, for 1907,

p. 773 *et seq.*; for 1907 and 1908, from the *Jahrbuch für den Oberbergamtsbezirk, Dortmund*, for 1909, p. 756 :—

Number of coke-ovens

with recovery of by-products—	1901.	1902.	1903.	1904.	1905.	1906.	1907.	1908.
At work . . .	1165	1663	2061	3015	3139	3603	3892	4007
In course of building . . .	1533	1346	1335	822	417	112	?	?

On the other hand, there were in 1903, 75,232 beehive-ovens at work, and 4940 in course of erection. In 1906, 5893 new beehive ovens were started for work, and 4407 were in course of erection.

Of the 3603 by-product coke-ovens working in the year 1906 in the United States, 1295 were on the Semet-Solvay, 1890 on the Otto-Hoffmann, 362 on the Rothberg, 56 (not working) on the Newton-Chambers system. The 112 ovens in course of erection were all on the Otto-Hoffmann plan. In 1907 there were erected at Gary (Indiana) 1000 by-product ovens in connection with new steel-works; 560 of these by Heinrich Koppers of Essen, who during the years 1906 to 1910 erected further 816 ovens on his system.

In Belgium already in 1905, 80 per cent. of all the coke was made in Coppée furnaces. Much slower up to recent years has been the development of the by-product coke-ovens in France (where that industry had been originated by the Carvès ovens!) and in Austria.

We shall not make the attempt to give a description of all the new coke-ovens patented during the last few years, more particularly since it would involve a corresponding number of diagrams; we shall merely give an enumeration of the different patents, along with a reference to the places where the descriptions are to be found, and we shall then select a few of the most important and most widely adopted plans for special description and illustration. We shall not give any account of such inventions as are only intended to utilize the coke-oven gases for heating-purposes, in order to increase the yield of coke. Special descriptions of that industry recently published are: *Modern Coking Practice*, by T. H. Beyrom and T. E. Christopher, London, 1910; *Neuerungen auf dem Gebiete der Nebenproduktenkokerei*, by Alfred Gobiell, Wien and Berlin,

1911; *Zusammenfassende Darstellung der Kokereitechnik*, by L. Herwegen, Gelsenkirchen, 1912.

Patents for coke-ovens with recovery of tar and ammonia have been obtained by:—

Ströhmer and Schultz (Ger. Ps. 13395 and 16807).

H. Aitken (B. P. 2682, 1882).

U. Hegener (Ger. P. 13996).

Th. Hornig (Ger. Ps. 21908 and 23670).

F. Lürmann (Ger. Ps. 13021, 15512, 16134, 16741, 17055, 17179, 17203, 17661, 18128, 18927, 20205, 20211, 22602, 29088, 29557, 31660).

L. Semet and E. Solvay (Ger. P. 18935). Experiments made with their ovens by Ch. Demant are described in the *Revue Universelle des Mines*, vol. xiii., p. 593; Wagner's *Jahresber.*, 1883, p. 1220.

G. Hoffman (Ger. P. 18795).

C. Otto & Co. (Ger. Ps. 13156, 16436, 16840, 19040, 20908, 24586, 31004, 31590, 34431, 37062). Their ovens will be described in detail below, as those most generally employed in Germany.

J. Jameson (B. Ps. 1947, 5076, and 5498, all of 1882; Ger. Ps. 24915, 25676, 27694). His coke-ovens are the most energetic attempts at combining the beehive-ovens with a recovery of the by-products, and will be described below.

A. Hüssener (Ger. Ps. 16923, 20196).

H. Simon (as communicated by F. Carvès: B. Ps. 544, 1883; 15920, 1884).

H. Simon and Watson Smith (B. P. 11967, 1883).

H. Hutchinson (B. P. 2843, 1883).

O. Ruppert (Ger. Ps. 24404, 26307).

R. de Soldenhoff (Ger. P. 25824; B. P. 11967, 1885).

A. Klönne (Ger. P. 25673).

Hiltawski and Kahnert (Ger. P. 24438).

Schlesische Kohlen- und Kokswerke in Gottesberg (Ger. Ps. 25825, 26421).

H. Herbertz (Ger. Ps. 15086, 17873, 25526, 27506, 31906, 34286).

Th. Bauer (Ger. Ps. 28530, 32235, 32660).

Th. Nicholson (B. P. 358, 1884).

C. E. Bell (B. P. 443, 1884).

J. McCulloch and Th. Reid (Ger. P. 31158).

A. M. Chambers and T. Smith (B. P. 4708, 1884; and B. P. 7358, 1885).

H. Stier (Ger. Ps. 26897, 35120).

F. Wittenberg (Ger. P. 26132).

A. Zwilling (Ger. P. 29888).

Gebrüder Röchling (Ger. Ps. 33956, 35001).

Lothringer Eisenwerke at Ars (Ger. P. 32841).

J. Quaglio (Ger. P. 36357).

J. Schmalz (Ger. P. 37182).

Descriptions of most of these patents have been collected by F. Fischer in *Dingl. polyt. J.*, vol. ccxlviii., p. 249; vol. ccl., pp. 456 and 521; vol. cclii., pp. 253 and 283; vol. ccliii., p. 372; vol. cclvi., p. 359.

These are translated in the *J. Soc. Chem. Ind.*, 1884, pp. 101, 505, 510, 531; 1885, p. 484.

A synoptic table of the ovens known up to 1884 has been given by Watson Smith, *ead. loco*, 1884, p. 605 (also in the *Journal of the Iron and Steel Institute* of that year, with a table of diagrams and many further particulars).

New English and American patents:—

Coke Oven Constructing and Working Company, Limited, and Brown (B. P. 29367, 1913).

Cochrane (B. P. 3856, 1914).

Duckham (B. P. 13936, 1914).

Summers (B. P. 10284, 1914).

Glasgow, comm. from Rusby (B. P. 22425, 1914).

C. H. Hughes (U.S. Ps. 1120146 and 1120147).

The following is a list of the German patents taken out since:—

Gebrüder Röchling, No. 38312.

J. Collin, No. 36518.

Dr C. Otto & Co., No. 37280.

F. Ströhmer, No. 46595.

Dr C. Otto & Co., No. 50982.

F. Brunck, No. 51518.

C. Otto and F. W. Lürmann, No. 52206.

W. Fritsch, No. 52134.

O. Dilla, No. 53860.



M. Kleist, Nos. 56488, 56489, 59635.  
 The Economic Gas and Coke Co., No. 59893.  
 F. Stauber, Nos. 61532, 67189.  
 J. Leschhorn, No. 67099.  
 G. Martin, No. 72103.  
 F. Brunck, No. 73504.  
 Th. Bauer, No. 73701.  
 G. Margirino, No. 78927.  
 C. Otto & Co., Nos. 80145, 82000.  
 T. J. Collin, No. 80820.  
 H. Stinnes, No. 88389.  
 C. Otto & Co. No. 90499.  
 Aktienges f. Kohlendestillation, No. 94040.  
 Wechselmann, No. 103508.  
 Festner & Hofmann, No. 103577.  
 Dillon de Micheroux, No. 104229.  
 Brunck, No. 107864.  
 Dr C. Otto & Co., No. 105432.  
                   Ditto           No. 106959.

Some more recent patents will be mentioned below.

Abstracts from these specifications and their English equivalents are given in the successive volumes of the *J. Soc. Chem. Ind.*

Very important papers on many of these coke-ovens, with exact diagrams, have been published by A. Hüssener (*Stahl u. Eisen*, 1883, p. 397), C. Otto (*ibid.*, 1884, p. 396), P. Lürmann (*ibid.*, 1892, p. 186), G. Hilgenstock (Glückauf, 1896, p. 497), R. Remy (*Z. angew. Chem.*, 1890, p. 327), A. Dannenberg (*ibid.*, 1894, p. 352), Truchot (*ibid.*, 1898, p. 263), Hilgenstock (*J. Gasbeleucht.*, 1902, 617), Beilby (*J. Soc. Chem. Ind.*, 1899, 643). A finely illustrated volume has been issued by the United States Coke and Gas Company, on *The Destructive Distillation of Bituminous Coal*, 1906.

#### *Description of some of the most important forms of By-product Recovery Coke-Ovens.*

We may with Watson Smith (to whose valuable contributions I am indebted for some of the following information) fitly class the various forms of recovery coke-ovens (as we shall style those

ovens which aim at the recovery of tar and ammonia) as being derived, consciously or not, from three "root-forms," namely—first, the beehive, a sort of covered-in meiler or mound, into which air is admitted so that some of the coke is burned as fuel for the remainder; secondly, the Coppée oven; and thirdly, the Knab-Carvès and Pauwels-Dubochet coke-ovens. The two latter belong to that class of coke-ovens which we may call horizontal closed ovens; both of them are so constructed that the gases evolved during dry distillation are utilized for heating the ovens from without, no air being admitted into the coking-chamber itself. The principal difference between the Coppée and Knab-Carvès ovens is as follows:—the former are provided with a large number of openings in the upper part of their side-walls, connected with an equal number of parallel heating-flues running perpendicularly downwards between each two ovens, and into these flues air is admitted, the flame ultimately passing below the sole. The Knab-Carvès ovens, as well as the Semet-Solvay ovens, are heated by flues running horizontally in a zigzag form, also between each two ovens.

The upright ovens of the Appolt system have also been adapted to the recovery of tar, etc.; but we shall not deal with these, as they do not seem to have been very widely used.

### *1. Modified Beehive-Ovens.*

To the beehive form belong the Meiler arrangements of Jones and of Blackwell, where tar and ammonia were collected by underground pipes, but the gases were passed upwards by the central stack and were lost. Real beehive-ovens, modified for the recovery of tar and ammonia, are those of Aitken and Jameson, which bear much resemblance to each other. Aitken blows air into his oven above the coke, along with the return gas from the condensing and scrubbing apparatus, and he exhausts the gases and vapours, drawing them downwards through the bottom of the oven by means of three perforated flues through which the gases and products pass, uniting in one main, before proceeding to the condensing-apparatus.

The special object of Jameson's invention (B. Ps. 1947 and 5076, 1882) was to utilize the existing beehive-ovens as much as possible, merely adapting them to the recovery of tar and

ammonia. He places an exhaust pipe with tap below the soles of his oven, and in addition to this he provides two other smaller pipes, through which the gases and vapours are returned at suitable intervals. The oven is filled as usual, and as soon as ignition has taken place above, the wider suction-pipe is caused to act gently, effecting a slow exhaustion of the by-products and gases. Since this process diminishes the quantity of the coke and makes it softer, Jameson conveys through the other pipes a portion or the whole of the gas drawn off, and a portion or the whole of the tar-vapours, to a similar oven, but one which has attained a further stage of combustion and ignition, in order that the carbon of the gases and vapours may become deposited in the pores of the coke thus treated, whilst the hydrogen burns at the surface of the mass or escapes. He claims various other possible modes of action and treatment of gas and by-products (such as the addition of pitch deprived of its valuable portions).

Jameson further proposes (B. P. 5498, 1882) to treat carbonaceous or coaly matters, shales, etc., difficult or impossible to coke, such as "duff-coal" or pit-heaps, also on the partial-combustion principle in an oven which partakes of the nature of a reverberatory furnace. It resembles a modified beehive-oven, with a fireplace and reverberatory-furnace fire-bridge attached, so that the flames from the furnace can play over the thick coking-mass on the deep-lying oven-bed, and then pass on to the chimney-flue, whilst the suction process for gases and by-products is set up in the space below the perforated bed on which the coking-mass lies. He also proposes to adapt this process to the roasting of ores in order to recover by-products, and for the recovery of fairly pure carbonic acid from limestone or in sublimation.

Particulars concerning the working of the Jameson ovens are given by the inventor himself in the *J. Soc. Chem. Ind.*, 1883, pp. 114, 228, and 405; and 1885, p. 314. He states a good many objections to the use of gas for heating coke-ovens from without, to which he prefers burning the surface coke by means of the downward suction employed. We will not enter into his theories, so many facts pointing the other way; his own ideas as to the use of the gas evolved in coking for other purposes were confessedly very imperfect.

The average yield per ton of coal is estimated by W. W. Pattinson at 10 lb. of sulphate of ammonia, 8 gall. of oil, and 12,000 cub. ft. of gas. The cost of plant per oven, that is, the addition of the new parts, varies from £10 to £20. The yield of coke is, "if anything, rather greater than in the ordinary oven," say 10 to 13 cwt. from one ton of Northumberland small coal, or  $67\frac{1}{2}$  to 70 per cent. from Durham coking-coal [in any case very much below that obtained with closed ovens of the Coppée or Carvès type].

In the paper read in 1885 (*J. Soc. Chem. Ind.*, 1885, p. 314), Jameson discusses the reasons why his process, although it fell into the hands of the ablest of practical men, and was worked out in a great number of places, with no regard to expense, had not realized the anticipations of its inventors and its promoters. Modifications are described for making the oven bottoms more nearly air-tight, and for cooling the gas in order to increase the yield of ammonia and oil.

We shall see further on that the *tar*, or rather (as Jameson himself calls it) the "oil," produced in the Jameson ovens is altogether different from gas-tar, being a low-temperature product, and is principally composed of paraffinoid hydrocarbons, such as exist in shale-oil, browncoal-tar, etc. But it is much less valuable than the latter; since its specific gravity is very high, there is very little chance of utilizing it for the manufacture of burning- and lubricating-oils, and the idea of "improving" it by passing it through red-hot tubes, as patented by C. E. Bell (B. P. 9510, 1884; extended to blast-furnace tar by B. P. 12681, 1884), and advocated by Armstrong (*J. Soc. Chem. Ind.*, 1885, p. 451), is thoroughly impracticable, as will be shown later on. Hence the Jameson tar must be regarded as of very little value.

There is also no doubt that the yield of *ammonia* from the Jameson ovens is not very high, decidedly less than from closed coke-ovens. Obviously the admission of air is very prejudicial in that respect, although the low temperature of the Jameson oven ought to favour the formation of ammonia in other respects. It is also evident that some of the ammonia is directly burned.

We will mention only one more attempt in a similar direction. H. Hutchinson (B. P. 2843, 1883) believes it possible to obtain at will hard coke along with tar rich in benzol by causing a rapid rise in the temperature of ignition, or a soft

coke along with tar rich in paraffin by slow coking. The former he proposes to effect by passing previously heated air through numerous channels or small flues into the ordinary coke-ovens, in order to hasten the coking and raise the temperature of ignition, the by-products being drawn off by flues in the upper part of the ovens. [That tar produced under such circumstances should be "rich in benzol" is very doubtful.] He also proposes producing heating-gas or illuminating-gas by passing, along with the air, superheated steam through a perforated tube rising in the centre of the oven amongst the fuel.

In any case we may here state it as an admitted fact: *that no coke-oven of the "open" kind, where air is admitted into the coking-chamber, yields tarry products similar to ordinary coal-tar—that is, such containing a considerable quantity of benzene, naphthalene, anthracene, and other aromatic hydrocarbons, employed as first materials in the manufacture of artificial dyes and colours.*

Some of the recovery-ovens retain the form of the *beehive*, but so modified that the oven becomes a closed one, no air being admitted into it, whilst tar and ammonia are evolved, all the heating being then done by the return-gas. This is the case with one of the ovens constructed by Pernolet, and also with that of Klönne (Ger. P. 25673). The latter draws off the gaseous products from the top and heats the bottom of the oven by the return-gases remaining after condensation, till all the tar and ammonia are drawn off as far as possible. Then the second stage of the process is started by conducting the gases, instead of through the hydraulic main, into a vertical side-flue, some air being admitted at the same time in front of the lower part of the oven, and the partially burnt gases being completely burnt later on by air previously heated. This oven thus forms a connecting link between open and closed coke-ovens; it does not seem to have been employed to any great extent.

The problem of adapting beehive coke-ovens to the recovery of by-products seems to have attained a better solution, by entirely doing away with the old method of coking by partial combustion of the coal, and applying all the heat from without by means of bottom-flues, the necessary degree of heat being attained by a previous heating of the combustion-air in Siemens's or other "recuperators." This is done in the

ovens patented by C. Otto & Co., and the Hibernia and Shamrock Coal Company, and erected in the Shamrock pit in Westphalia in 1886 (Ger. P. 37280). There are two recuperators placed side by side in the wall, between two sets of coke-ovens. One of these stores up the heat of the fire-gases passing through it, while the other transmits the heat, already received, to the air which is to maintain the combustion of the residual gases in the bottom-flues. Once an hour the direction of the draughts is changed, so that the two recuperators mutually exchange their mode of working. The gases given off in the coking-chambers are drawn off by a pump, and forced back into the flues below the soles of the ovens. Between the escape-pipe, which is situated in the crown of the oven, and the pump, there is a hydraulic main, and the usual condensing and scrubbing arrangements, just as constructed for the Coppée-Otto ovens (pp. 105 *et seq.*). At the Shamrock pit each oven holds a charge of 4 tons, and gets through it within 55 hours; the yield is 80 per cent. of large-sized coke (against 65 to 68 per cent. obtained by the old process), 5 or 6 per cent. of tar, and 1 per cent. of sulphate of ammonia; also 244 cubic metres (say 8540 cubic feet) of gas per ton of coal. The quality of the coke is altogether as good as that of the ordinary beehive coke; the reason why this is the case, in spite of the heat being exclusively communicated by means of bottom-flues, is probably connected with the fact that the coal is spread in a comparatively shallow layer over the oven-sole, and the very large increase of yield is hence an entire gain. Besides this, the time occupied in coking the charges is very much reduced, and the by-products obtained are a further gain.

According to information derived from competent sources, it appears that the object of the above-described invention is solely the better utilization of existing beehive-ovens, by adapting them to the new system (which is a rather expensive process); but nobody would think of building ovens of this kind without regard to the tar produced, for the simple reason that the discharging of beehive-ovens is decidedly more troublesome than that of horizontal coke-ovens. Nobody in Westphalia seems to doubt that the latter are the best coke-ovens, and that beehive-ovens will be discontinued altogether in the course of time.

*II. Recovery-Ovens on the modified Coppée System.*

A very remarkable oven of this class is that of Lürmann, differing from all others in the continuous style of work adopted in it.<sup>1</sup> The oven, which, like all other Coppée ovens, forms a narrow channel of moderate height and of considerable length (say 30 ft.), consists for two-thirds of its length of a heating- and coking-chamber, and for the last third of a storage-chamber. The front of the first chamber is closed by a door in the shape of a ram, moved alternately backwards and forwards. The coal to be charged falls down from a hopper in front of the ram, and is by this pushed into the oven, forcing on the charge already contained in the oven towards its other end, where the finished coke collects and is taken out by a discharging apparatus. The gases and vapours pass away from the centre of the coking-chamber through a hydraulic main, and, after condensing the tar and ammonia, are used for heating the coking-chamber from without, the thickness of the walls being reduced to  $2\frac{1}{2}$  or 3 inches, the numerous partition-walls of the flues bracing them up to a sufficient extent. The whole is always under a considerable pressure, produced by the ram. The cooling of the walls during the charging and discharging, unavoidable in all other ovens, is here done away with, as the same quantity of coal is always in the same stage of distillation, the quantity and quality of the gas is invariably the same throughout the process; the details of the construction are such that a very high temperature can be maintained at will all over the coking-chamber. Owing to this and the high pressure, it has been found possible in the Lürmann oven to make hard smelting-coke from very dry, anthracite-like coal, the smalls of which are otherwise of hardly any use; but it is best to mix this with half its weight of ordinary coking-coal. It is not adapted to coking-coal without the admixture of dry coal. It would seem from this description as if the Lürmann ovens were the most perfect of their kind, at least so far as the coking proper is concerned, and a goodly number of them have actually been erected in Westphalia; but they have not answered their purpose, and have been stopped,

<sup>1</sup> I take the description and criticism of this oven from Hüssener, *Stahl u. Eisen*, 1883, p. 401, where a good diagram is also given.

as the quality of the coke was not satisfactory and the discharging-apparatus showed serious drawbacks. Lürmann, in the discussion following the reading of the paper (*Stahl u. Eisen*, 1883, p. 412), points out that his oven is not intended to compete with those destined for the ordinary descriptions of coking-coal; that it produces excellent coke from coal which is otherwise quite unfit for that purpose; that this coke is especially good for cupola-furnaces (as proved by certificates); and that his ovens yield tar and ammonia from coals otherwise useless for coking-purposes. It would appear that the quantity and the quality of the tar and ammonia recovered in Lürmann's ovens have not been at all accurately ascertained, and we must therefore dismiss them for the present from our consideration.

Otto's first modifications of Coppée's oven for recovery purposes have been superseded by his later adoption of Hoffmann's principle, noticed below. We also refer the reader to the patent specifications and to the extracts in *Dingl. polyt. J.*, as those given by Watson Smith, for the ovens patented by Herbertz, R. de Soldenhoff, and others, belonging to this class, none of which have met with an extensive application.

*The Otto-Hoffmann Oven.*—The most successful kind of oven, as regards the number introduced and the results obtained in Germany, is that originally patented by Gust. Hoffman (Ger. P. 18795), based upon a proposal of Th. von Bauer, and modified by Dr C. Otto & Co. by a number of additional patents (*cf.* p. 97). The essential feature of this plan is a combination of Siemens's recuperators with the ordinary Coppée oven, provided with a number of improvements in details. The following is a description of these ovens, principally from the paper, published by Otto in *Stahl u. Eisen*, 1884, p. 396, but with modifications to suit later patents; the diagrams are taken from the working drawings kindly lent to me by Dr Otto.

Fig. 8 is a longitudinal section through the centre of an oven; Fig. 9 a longitudinal section through the flues between each two ovens; Fig. 10 a tranverse section through a number of ovens. The letters show the same parts on all the diagrams.

These ovens are from 30 to 33 ft. long, 2 ft. wide, 5 ft. 3 in. high to the abutment of the arch, with a 4-in. taper, and 2 ft. 11½ in. from centre to centre. In lieu of the side openings through which, in ordinary Coppée ovens, the gases



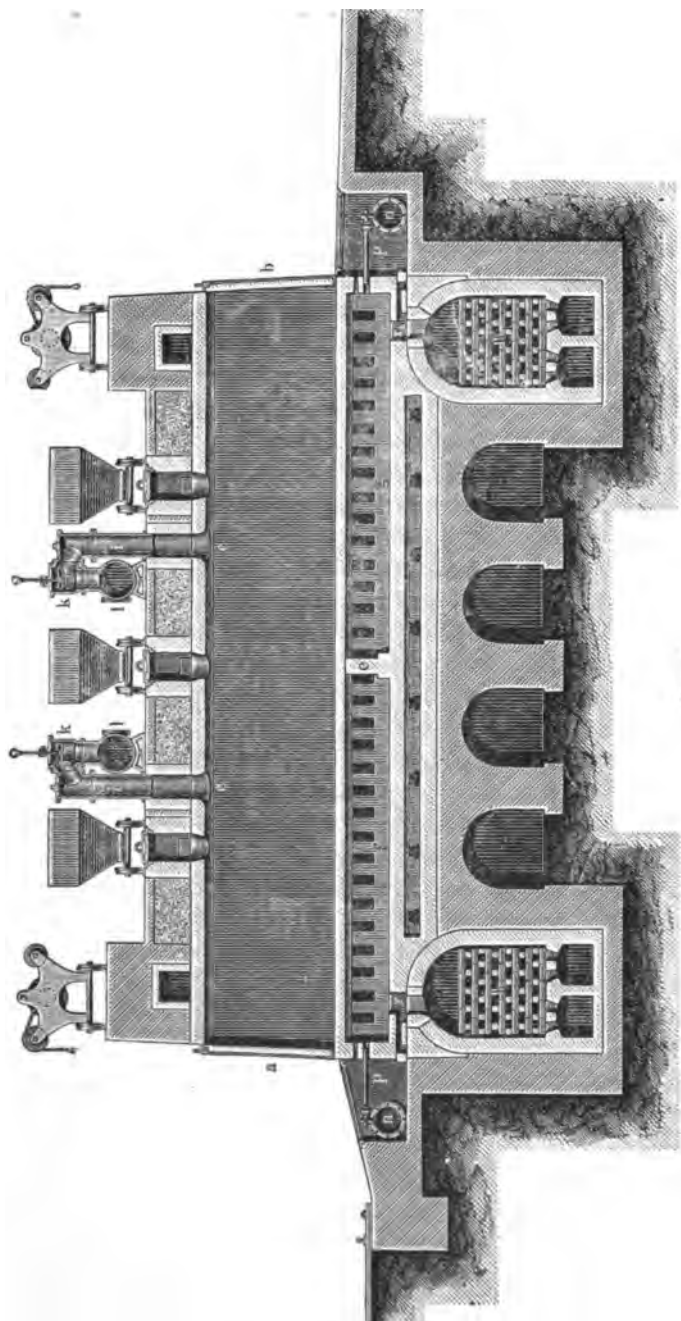


FIG. 8.

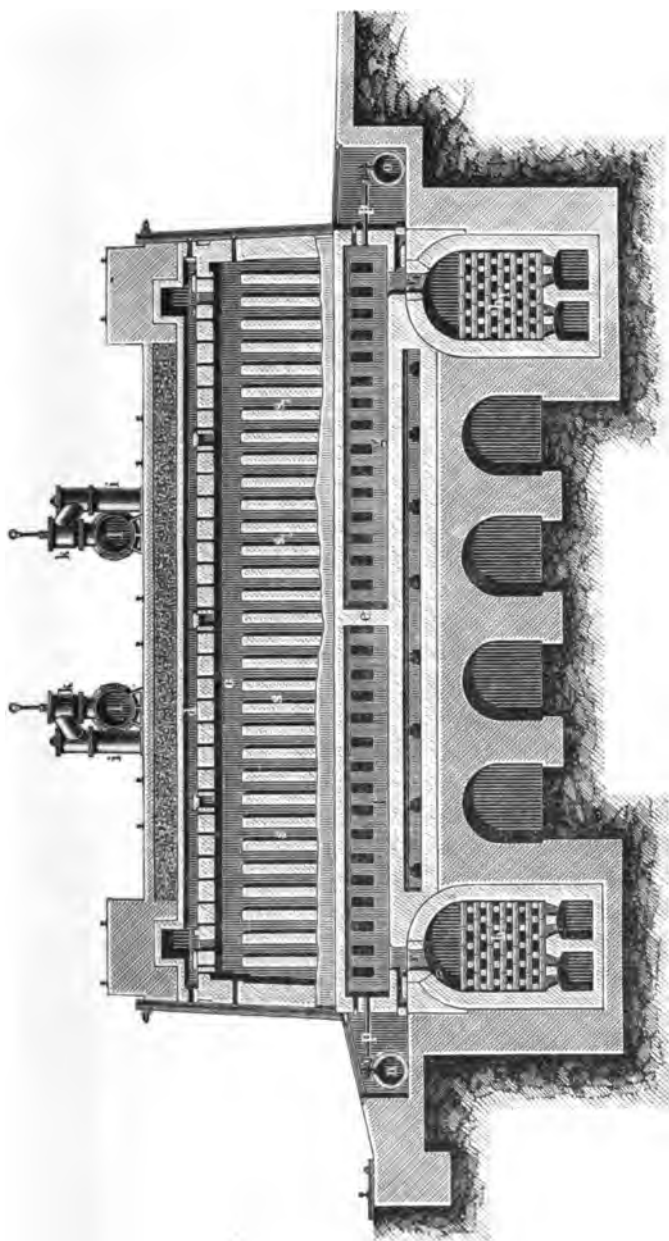


FIG. 9.

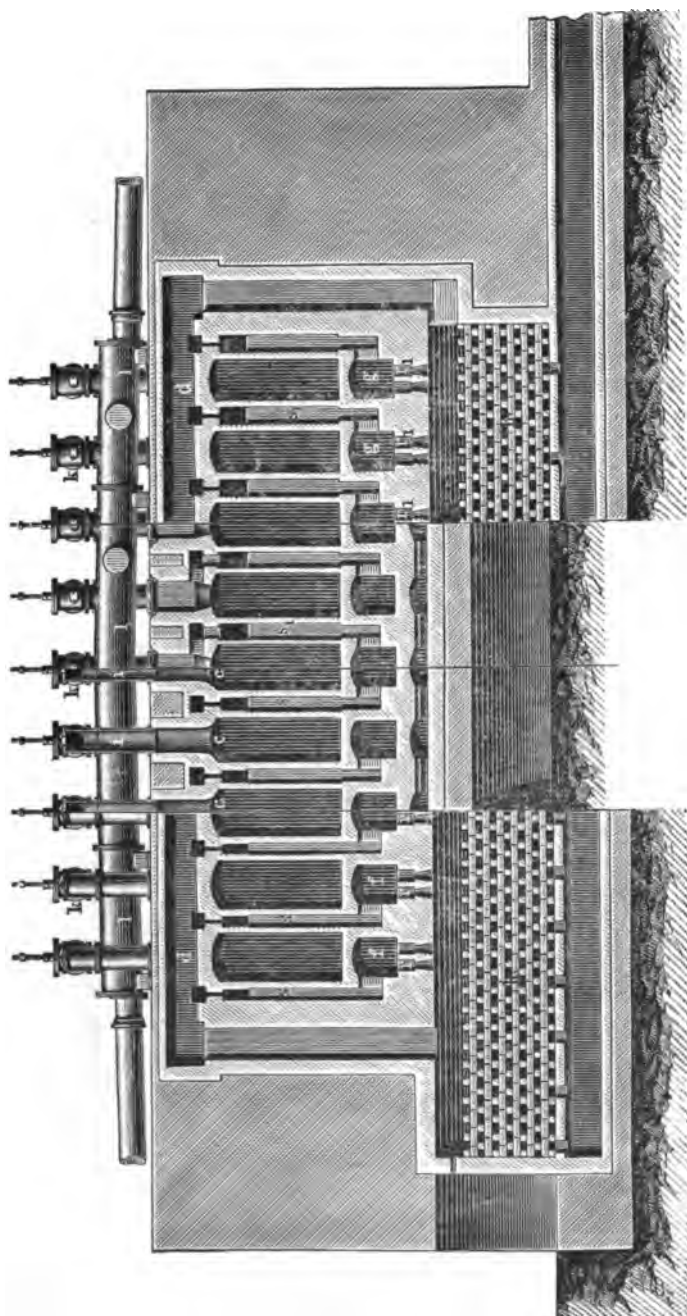


FIG. 10.

pass out of the coking-chamber down the sides and underneath the bottom, in order to be burnt, there is here no direct connection between the coking-chamber and the side of the oven; apart from the end doors for charging and discharging (*a* and *b*), closed during the operation, there are only two openings in the top arch, *c c*, through which the distillation gases and vapours can escape. In the side-walls below the abutment there is a horizontal flue, *d*, passing along all the vertical side-flues and connecting them. Each bottom-flue in the length of the oven is divided midway by a partition, *e*, in two equal halves, *f* and *g*. Each of these half-flues communicates with a recuperator, *h* or *h*<sub>1</sub>, destined for heating the air necessary for the combustion of the heating-gas. The recuperators are long chambers, filled with an open network of bricks, and reaching along the whole range of ovens. At the end of the range the two recuperators, *h* and *h*<sub>1</sub>, by means of a throttle-valve, are made to communicate either with the fan-blast conducting air or with the chimney.

When the ovens have been charged and the coking is in progress, the gases evolved from the coal escape through the openings *c c* in the oven-arches into the tubes *i i*, and then pass into the main receivers *l l*, the valves *k k* being left open. From the receivers *l l* the gases pass to the condensing-plant, where they are freed from tar and ammonia in the gas-coolers and in the scrubbers, as will be described below. The same exhauster which drew the gases to the condensing-apparatus now forces them back towards the ovens into the tube *m*; and from this, according to the position of the throttle-valve, either into the tube *n*, on the one side of the oven-range, or into the tube *o*, on the other side of the range. At each oven the tubes *n* and *o* communicate with the bottom-flue *f* and *g* by means of a small inlet-pipe, *p*, provided with a tap.

Suppose the gas is passed into the pipe *n*, on one side of the oven-range, the throttle-valve of the recuperators is placed so that the air (which is forced in by means of a fan-blast) enters at the same side into the recuperator *h*, which communicates opposite each oven, by openings, *r r*, with the bottom-flue *f*. Thus both gas and heated air enter into the bottom-flue *f*, the combustion taking place partly in this flue, partly further on. The current of burning gases and very highly-heated combustion products passes upwards by the parallel vertical flues *s* into the upper

horizontal flue  $c$ , and on the other side of the ovens by the parallel vertical flues  $s_1$  downwards into the bottom-flue  $g$ , from which the gases, now completely burned, pass through the recuperator  $h_1$  into the chimney, and on their way give up their heat to the network of bricks. After a certain time, say an hour, the throttle-valves are reversed, and the gaseous current now travels in the opposite direction: the return-gas from the condensing-plant enters into the tube  $a$ , the air into the recuperator  $h_1$ , the combustion takes place in the bottom-flue  $g$ , the products pass through the vertical flues  $s$ , upwards into  $c$ , and thence through the vertical flues  $s$  downwards into  $f$ , and at last through the recuperator  $h$  into the chimney.

Dr Otto points out that, owing to the slow conductivity for heat of fire-bricks, the air in Siemens's recuperators, worked alternately in opposite directions, is heated incomparably more quickly and highly than in those recuperators where the hot combustion-products travel on one side, the air is heated on the other side of a brick partition, and the current of gases always flows in the same direction.<sup>1</sup> In the Otto recuperators the temperature of the air rises to  $1000^{\circ}\text{C.}$ ; and the effect of this is that the cold gases, deprived of their tar, as they return from the condensing-plant, are far more than sufficient for carrying out the coking-process. If they were all to be burned, the ovens would get much too hot; and it is found that there is an excess of 200 cubic metres (say 7000 cubic feet) of gas per oven per day which can be utilized in other ways. With a normal charge of 115 cwt. of dry coals per oven the coking-process is finished in 48 hours, but sometimes less, so that the quantity of gas must be diminished to bring the time up to 48 hours. Since both gas and air are blown in mechanically, it is quite easy to regulate the process at will.

The quality of the coke made in these ovens is altogether excellent; the yield considerably exceeds that formerly got from the same coal in Coppée ovens, without recovery of tar and ammonia. Calculated upon coal containing 10 per cent. water, it was formerly 61 per cent., and is now 68 per cent.; that is, upon dry coal, 67.7 and 75.56 per cent. respectively. Dr Otto attributes this result to the absolute air-tightness of the ovens, along with a slight over-pressure. The temperature, as measured

<sup>1</sup> This is contradicted by Simon, *cf.* below.

by a Steinle and Hartung's graphite pyrometer and controlled by the fusing of metallic alloys, was found to be 1200° to 1400° C. in the bottom-flue, 1100° to 1200° C. in the side-flues; 1000° in the recuperator at the time the air-current is admitted, and 720° when it is shut off; 420° in the chimney.

Of the Otto-Hoffman ovens, as described just now, up to 1894 already over 1200 were erected on the European Continent, more than three times as many as existed there of any other type of by-product oven. In 1894 they were introduced into America by the Otto-Coke and Chemical Company, and later on by the United Coke and Gas Company. Up to 1905, 2780 of these ovens had been built by them in various States of the Union, the surplus gas being used for fuels, power, and illumination. The United Coke and Gas Company, New York, claim that the surplus gas from their ovens gives a higher candle-power from the gases of coal than can be obtained when the coal is distilled in the ordinary gas retorts. They apply to the gas a system of coolers and washers similar to that which is usually employed for blast-furnace gases (see later on). Schniewindt (*J. Gasbeleucht.*, vol. xliii., p. 53) makes more detailed communications on this system which is said to work most successfully, the "rich" and the "poor" gas being purified in quite separated sets of apparatus.

The "Rothberg" oven is of a similar type. In 1904, 94 of these were in operation at Buffalo, and 141 in course of construction.

#### *Otto-Hilgenstock Ovens.*

In the course of time the Otto ovens have been improved in many respects, as to the more regular distribution of the heat, speedier finishing of the charge, and greater freedom of the masonry from repairs. We cannot go into details about these improvements, concerning which reference must be made to the above-enumerated patents.

We must, however, give the description of a coke-oven, later on patented by Messrs C. Otto & Co. (Ger. P. No. 88200), in which the recuperator is abandoned and heating by gas from the bottom is introduced. According to authoritative information, these ovens, known as the Otto-Hilgenstock ovens, of which up to the end of 1897 already 400 had been erected,

do considerably better work than the former constructions, owing to the production of heat taking place all along the length of the oven. The air for combustion is in a very simple manner heated in the foundation of the oven, so that no heat is lost there. There is no necessity for blowing in the air by machinery, and the gas is under such low pressure that all conditions are present for a good recovery of the by-products. The gas is conveyed in piping, laid underneath the ovens in an accessible way, and is from there introduced into the heating-flue by tuyeres. As shown in Figs. 11 to 13, the walls forming the foundation are conveniently arranged so as to run parallel to the length of the ovens, and are covered with an arch for each two ovens. The passages and flues, arranged in the foundations, are large enough to be accessible to workmen. In these passages are placed the gas-pipes *g*, with their tuyeres leading into the heating-flues; each gas-pipe supplies four lateral flues. The vertical through-going flues, *w*, force the heating-gases to travel within the partition-walls. The air for combustion can be introduced by an opening in front of each gas-burner, where it is forced in by an injector-action of the gas, or else by special flues for each oven, *p*, from the passage *L*. The heating up takes place by a side-valve, *v*<sup>1</sup>, through which the gas enters into the main flue when the valve *v* is shut. Since all the gas-inlets are accessible from below, the heat can be exactly regulated all over the oven, and can, for instance, be increased at the two ends without overheating the oven, which causes a more regular and quick heating without too much action on the brick-work. As the heat is greatest near the bottom, there is no danger of overheating the gas collected in the upper part of the ovens and thus destroying part of the by-products. The gas-pipe, placed in the foundation, is well protected, and does not interfere with the work on the top of the ovens. The subterranean passages also serve for heating the air previous to combustion, and thus utilize the heat radiating below. As the heating gases have a shorter distance to travel than with other systems, there is neither an excessive pressure at their entrance nor a vacuum at their leaving the ovens; hence any leakage of gases into or out of the ovens through joints and crevices is avoided, the quantity of by-products is increased, and the oven-gas is not contaminated with fire-gases. In all

these respects the new ovens work better than those provided with recuperators.

A detailed report on the Otto-Hilgenstock ovens, erected

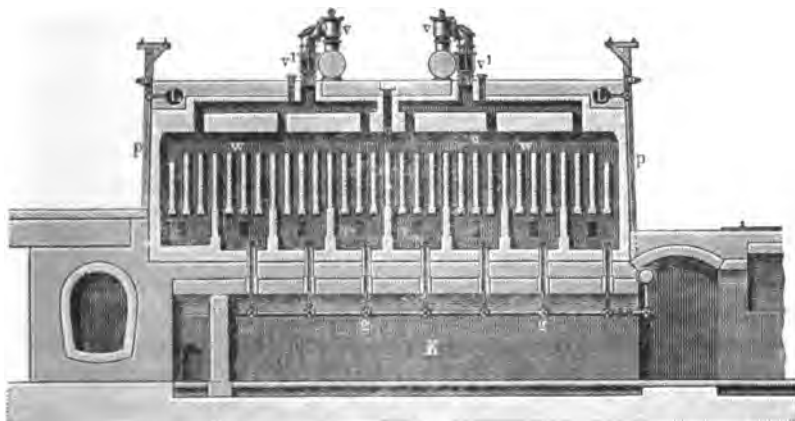


FIG. 11.

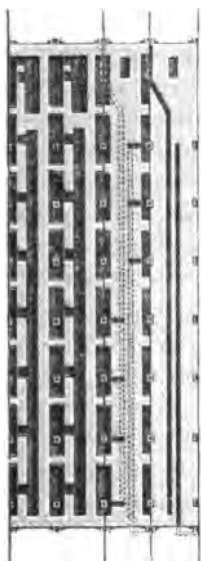


FIG. 12.

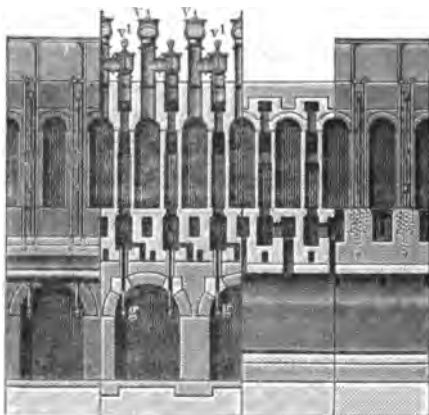


FIG. 13.

at a colliery at Rhenish Prussia, is made by Bertelsmann, in *Z. angew. Chem.*, 1899, p. 1098. There are 30 ovens, with double walls, 33 ft. long, 19.7 in. wide at one end and 23.6 in. at the



other (where the coke is drawn). Each charge is about 7 tons of coal, with 14 per cent. water, and requires 30 to 32 hours for finishing. The heating is performed by eight Bunsen burners from below; the temperature just above the burners is from  $1300^{\circ}$  to  $1400^{\circ}$ . The fire-gases rise perpendicularly and then travel towards the centre, where the temperature is  $200^{\circ}$  or  $300^{\circ}$  below the initial one; they are then taken downwards below the bottom of the coking-chamber and are then, with about  $1000^{\circ}$  C., employed to raise steam in four boilers, producing daily 140 tons steam of 8 atmospheres. The gases evolved in the distillation of the coal are cooled by air and water down to  $30^{\circ}$  C., washed with weak ammoniacal liquor, deprived of their tar by a Pelouze and Audouin apparatus (p. 58), and by another washing deprived of the last traces of ammonia. They are then collected in a gas-holder, from which they are conveyed to the ovens as fuel for these. About 1000 cub. ft. of gas are produced from 100 kg. of dry coal, on an average containing 2.5  $\text{CO}_2$ , 3.5 heavy hydrocarbons, 0.8 O, 7.6 CO, 27.2  $\text{CH}_4$ , 50 H, 8.4 N per cent. This gas has a fair illuminating power and a heating-value of 4300 to 4500 metrical calories.

Several recent patents of the firm C. Otto & Co. contain improvements of the process. Thus, according to Ger. P. 171901, of 1903 (issued in 1906), a saving is effected by shutting off the heating gas from the heating flues entirely or partly before the coking process is finished. Thus only the outside portions of the coal are coked by heat from without, and these coke the inside portions by communicating their heat to them. Their Ger. P. 214947 describes improvements of the Bunsen burners and of the charging-funnels.

Spilker (*Kokerei und Teerprodukte der Steinkohle*, 1908, pp. 18 *et seq.*) describes in full detail the starting, working, and discharging of these coke-ovens.

Hilgenstock (*J. Gasbeleucht.*, 1902, 617) points out the advantages which the new ovens, fired from underneath, have over the older Otto-Hoffmann and other ovens where the recuperator principle is employed, and in consequence of this the temperature must vary from  $1000^{\circ}$  to  $1300^{\circ}$  and backwards, each time the direction of the gases is changed. This must lead to a loss of tar and ammonia, as proved by a number of analyses made of the products of both systems.

A similar combination is the "United-Otto Coke-Oven" (U.S. Ps. 673928 and 644369), which claims to be the most efficient type of this kind, the coal being handled by machinery from the time it is unloaded from the car into the elevator until it is in the oven, the crushing (where necessary) being done in the same way. The quenching of the coke is also done in an ingenious manner. We must refer for these details (which hardly belong to the scope of this treatise) to a splendidly illustrated treatise on the Destructive Distillation of Bituminous Coal, issued in 1906 by the United Coke and Gas Company, 17 Battery Place, New York.

Short, in *J. Gas Lighting*, 1907, 97, gives a survey of the results obtained with Otto-Hilgenstock ovens, working with Durham coal. We quote from it merely the figures showing how the nitrogen and the sulphur of the raw material appear in the products:—

	Nitrogen, per cent.		Sulphur, per cent.
Contents of coal . . .	1.57 = 100		0.824 = 100
Left in coke . . .	0.68 = 43.31		0.598 = 72.53
In tar . . .	0.047 = 2.98		0.012 = 1.45
„ ammonia . . .	0.238 = 15.16	as H <sub>2</sub> S	0.198 = 24.00
„ cyanides and sulpho- cyanides . . .	0.0223 = 1.43	{ other compounds }	0.013 = 1.72
„ the gas, and loss . . .	37.12	loss	0.30

A modern Otto coke-oven holds about  $7\frac{1}{2}$  tons of coal, which are coked in 36 hours. The yield from Westphalian coal averages 72.2 per cent., so that each oven produces 1100 or 1200 tons of coke per annum (Haarmann, p. 4). The average production in 1900 in Westphalia amounted to 1260 tons per oven from recovery ovens, against only 890 tons from the old open ovens, and in the most modern recovery ovens even 1800 tons are reached (Haarmann, p. 6).

The condensing-plant belonging to the Otto ovens will be described in a later section of this chapter, where also the composition of the gas will be quoted. In this place we speak only of the composition of the tar.

*Tar* and *ammoniacal liquor* are separated by settling in large tanks. If the liquor is not strong enough for sale or for working up in the distilling-apparatus, it is used over again in the scrubbers till it comes up to 4° or 5° Twaddell, when it contains

about 1·7 to 1·8 per cent.  $\text{NH}_3$ . Westphalian coal yields about 14 per cent. of liquor at  $4^\circ$ , equivalent to a yield of 1 ton of sulphate of ammonia per 100 tons of dry coal. In the Saarbrücken district the yield is only 14 to 16 cwt., in Lower Silesia 16 to 18 cwt., in Upper Silesia 26 up to 34 cwt. per 100 tons of coal.

The yield of *tar* differs a good deal, according to the quality of the coal and to the efficiency of the cooling-apparatus; it may vary from 2 to  $3\frac{1}{2}$  tons per 100 tons of coal.

The following analyses were made in April 1886 of tar obtained from the same coal (A in a gas-works in ordinary retorts, B from a set of Otto's coke-ovens):—

	A. Gas-tar.	B. Coke-oven tar.
Water . . . . .	2·9	2·2 per cent.
Light oil up to $200^\circ$ . .	4·0	3·4 „
Benzol for aniline . .	0·92	1·1 „
Solvent naphtha . . .	0·20	0·32 „
Creosote oil . . . .	8·6	14·5 „
Crude naphthalene . .	7·4	6·7 „
Anthracene oil . . .	17·4	27·3 „
Pure anthracene . . .	0·60	0·70 „
Pitch . . . . .	58·4	44·3 „
Carbon . . . . .	15 to 25	5 to 8 „

The expenses incidental to the recovery of the tar and ammonia are not considerable; they consist principally of the cost of pumping the (rather large) quantity of cooling-water, the ammoniacal liquor, etc.; the cost of labour and repairs is very slight.

The following figures respecting the cost of erecting and working the Otto ovens have been supplied to the author by the inventor. The cost of erection naturally varies a good deal according to the situation. On an average it may be taken at 3050 marks (say £150) per oven for the ovens themselves, and 6000 marks (not quite £300) per oven for the very extensive condensing-plant, gasholder, Feldmann's apparatus for ammonium sulphate, etc. This also includes duplicate engines, pumps, and exhausters, and substantial buildings for all these erections.

A battery of 60 ovens converted in six months' time 3073

truck-loads of 10 tons of coal each into coke, and yielded at the same time:—

	Per 100 kg.	
915,245 kg. tar (say, 3 per cent.) . . . . .	M. 2.30 =	M. 21,050.63
313,446 kg. ammonium sulphate (1.02 per cent.) at M. 23 =		72,092.58
		M. 93,143.21
<i>Deduct</i> Sulphuric acid 313,446 kg. at 3.80 =	M. 11,910.95	
" Wages . . . . .	9,326.26	
" Salaries . . . . .	2,936.97	
" Sundry materials . . . . .	2,571.50	
		26,745.68
Leaving per 6 months a profit on tar and ammonia =	M. 66,397.53	
" 12 " " " "		M. 132,795.06
	Or, say,	£6600.

That is to say, each oven has coked per annum 1020 tons of coal, and the extra profit on tar and ammonia per ton of coal has been M. 2.16 (say, 2s. 9d.).

At the Burbacher Hütte in Rhenish Prussia in 1907 a set of 126 of the Otto-Hilgenstock ovens has been erected. The coking takes 36 hours. Tar and ammonia are condensed. The waste heat is utilized for 14 Cornish steam-boilers, with about 100 sq. ft. heating surface each. The surplus gas, moreover, amounts to between 60 and 90 cbm. per ton of dry coal, according to the amount of water contained in the fresh stock charged. This gas, possessing a heating-value of 5000 metric calories per cubic metre, serves for driving a gas-engine of 1200 h.p. for the electric central plant; part of the excess of gas is burned under steam-boilers and serves for driving a gas-turbine of 1200 h.p.

*Other ovens of that class.*—Th. von Bauer, who had suggested to Hoffmann one of the important principles of the above-described ovens, has himself worked out his ideas in a different way, better adapted to the wants of smaller works and to the employment of less bituminous coals (Ger. Ps. 28530, 67275, 73701). Since 1887 many hundreds of these ovens have been erected in the Creuzot works, thereby enabling an addition of an equal proportion of anthracite to be made to bituminous coal, whilst formerly only 20 per cent. anthracite could be used. Bauer subsequently worked out his principle in the shape of circular batteries, viz., horizontal ovens for

very bituminous coal, half-horizontal for semi-bituminous, and upright for non-bituminous. For the latter the tar and ammonia recovery-plant can be cut off at will, when the first period of work is over. Kassner (*Chem. Zeit.*, 1898, p. 993) discusses the results of Bauer's ovens in detail.

The oven constructed by J. W. Nienhaus (Ger. P. No. 94016) aims principally at avoiding an insufficient coking at the ends of the ovens. For this purpose he places the first partition of the heating-flue at the burners *n* on both sides of the oven, Fig. 14, only 8 in. from the ends, whilst the other partitions

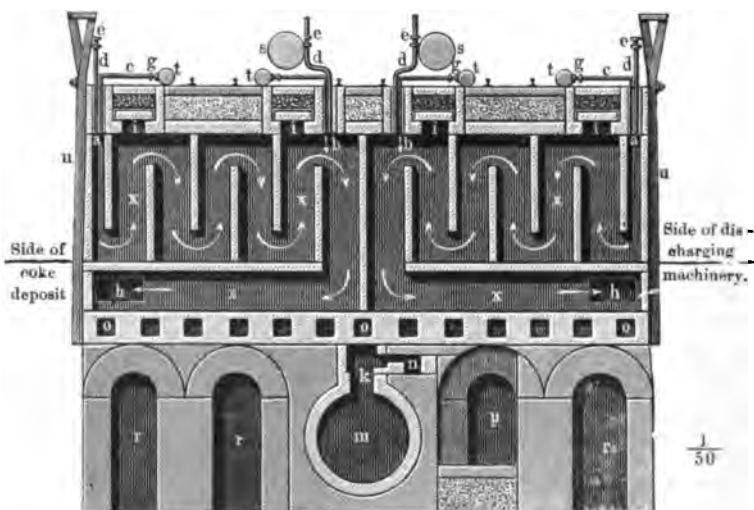


FIG. 14.

are 22 in. distant one from another. Thus the fire-gases, before entering the longitudinal walls, first quickly heat the outer ends, and this compensates the loss of heat occurring there by radiation. This also causes the expansion of the ovens to be quite even, and thus increases their durability. These ovens can also be worked for a considerable time without recovery of the by-products, and yet remain fit to take up the latter at any moment.

Nienhaus contends that in all coke-ovens with vertical flues the upper portion is not sufficiently heated; the charge is more quickly finished below than above, and this has a deteriorating effect on the output and the quality of the product. Nienhaus

therefore heats the ovens from above, the gas, as well as the previously heated air, being passed into the various combustion-chambers by tuyeres. The air for combustion is aspirated by the chimney, and, like the heating-gas, can be regulated by a tap for each chamber, so that the rate of combustion can be checked in all parts of the oven by means of the Orsat testing-apparatus.

### III. *Recovery-Ovens on the modified Carvès System.*

In the introductory part of this chapter (pp. 89 *et seq.*) we have spoken of the former stages of this process, namely, of Knab's, Carvès', Pauwels-Dubochet's, and Pernolet's ovens. Since attention had been drawn to the undoubted success of Carvès ovens, first by Angus Smith, then by H. Simon and others, there have been quite a number of "modifications" of the Carvès' ovens, as Hüssener's, Carvès own (generally called the Simon-Carvès oven), Ruppert's, Semet and Solvay's, Siebel's, the Gottesberg Coal and Coke Company's (*cf.* list of patents, pp. 96 *et seq.*).

Most of these systems have met with only a very restricted application; and we shall confine our description to those which have been more widely introduced, namely, Hüssener's and the "Simon-Carvès" oven, both of them (like some of the others) based upon a previous heating of the air required for combustion (a feature which we have also seen to be the essential point of the Hoffmann-Otto system), and the Semet-Solvay ovens.

The Carvès ovens have been considerably improved by the introduction of recuperators, patented in 1883 (No. 554) by Henry Simon as a communication from François Carvès.<sup>1</sup> Figs. 15 to 19 show the arrangement. Fig. 15 is a longitudinal section through a coking-chamber and cross-section through the external air and smoke-flues on line  $\alpha \beta$ , Fig. 17. Fig. 16 is a longitudinal section through the partition-wall of the coking-chambers on line  $\gamma \delta$ , Fig. 17. Fig. 17 is a part plan and part sectional plan of the coking-chambers and flues. Fig. 18 is part front elevation and part cross-section; Fig. 19 a sectional plan

<sup>1</sup> I take the diagrams in the text partly from the patent, partly from detailed unpublished drawings kindly supplied to me by Mr Henry Simon.

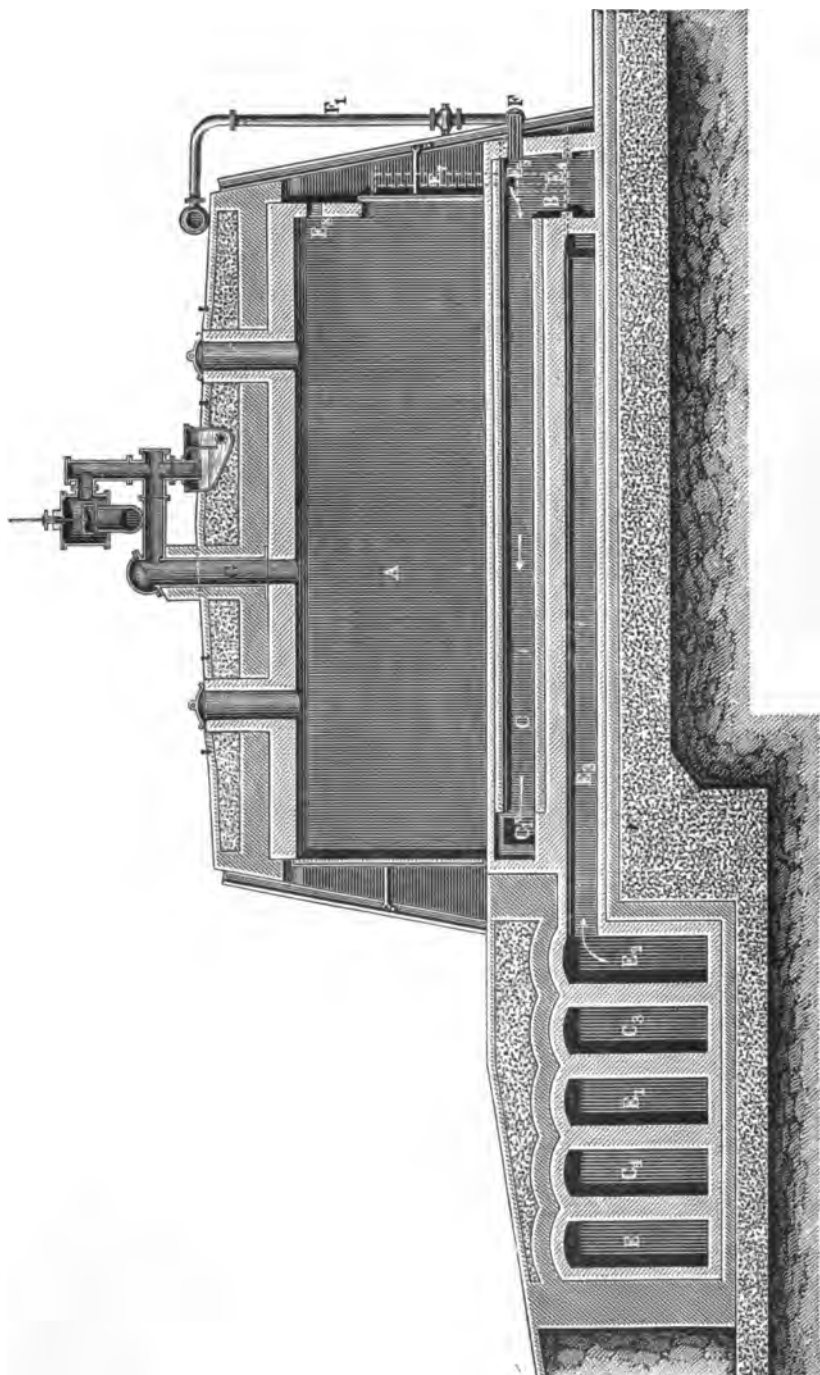


FIG. 15.

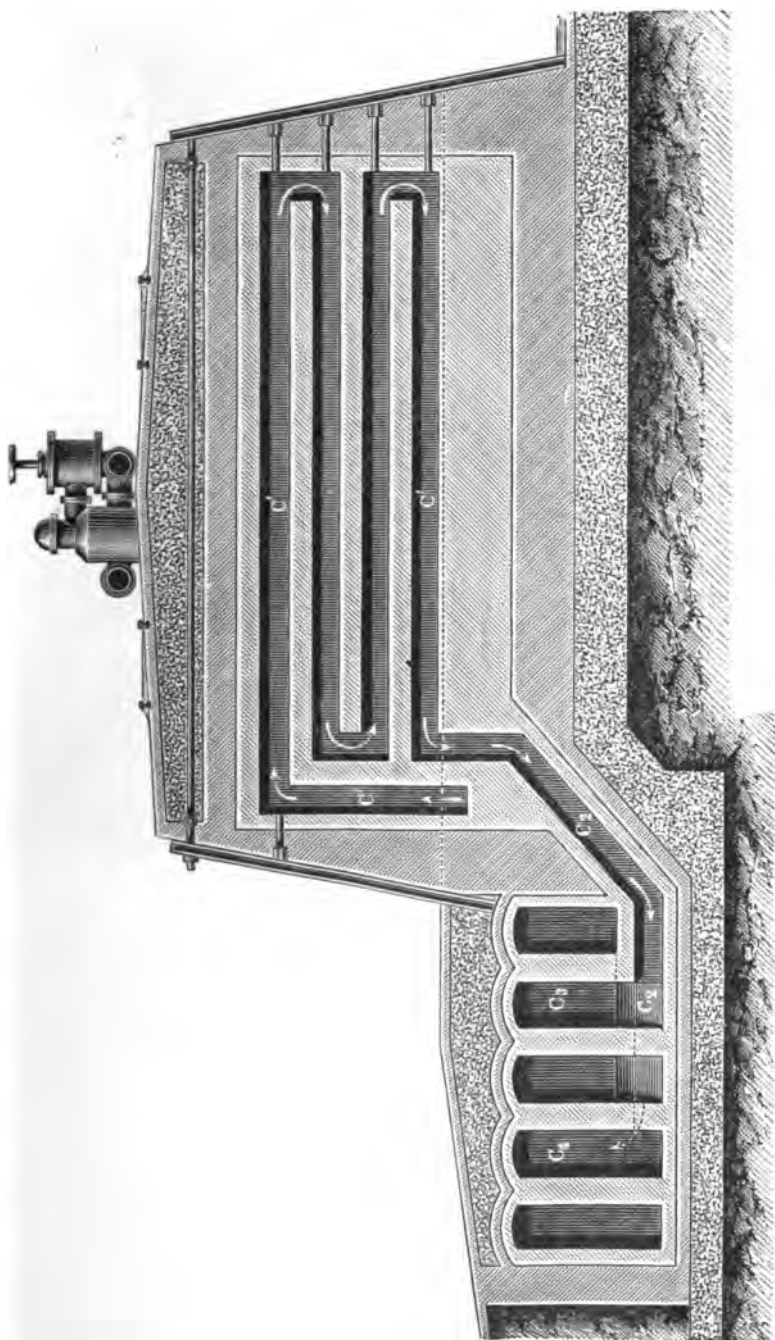


FIG. 16.





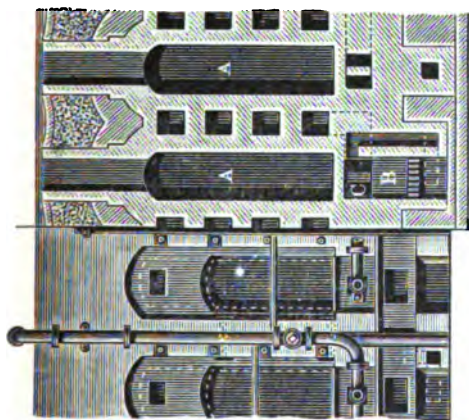


FIG. 18.

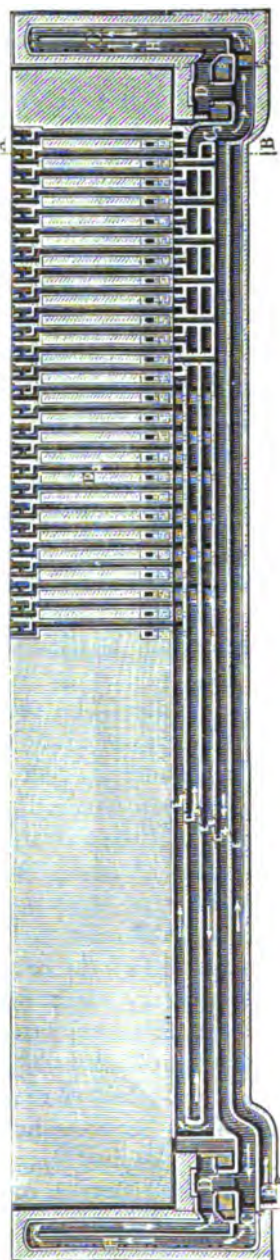


FIG. 19.

on a smaller scale of the smoke-flues and air-heating flues. We notice the coking-chambers A A (18 to 20 in. wide), the fireplace B with flue C leading thence under the oven-floor to the opposite end, where it passes laterally into the flue  $C_1$  in the side-wall of the chamber, first rising to the upper part of the wall, then descending in a zigzag direction (Fig. 16), and then down the inclined flue  $C_2$  into the external smoke-flues  $C_3$   $C_4$ . These flues, as will be seen from the plan, Fig. 19, extend along the whole range of the coking-chambers, each flue being closed at one end and communicating with the chimneys D  $D_1$  at the other. The flues  $C_1$  communicate alternately with the flues  $C_3$   $C_4$ , so that the combustion-gases of one half of the range of ovens are discharged into the flue  $C_3$  and those of the other half into  $C_4$ , the flow of such gases towards the chimneys D  $D_1$  taking place in contrary directions in the two flues. An air-flue, E, extends first along the outer side of the flue  $C_4$ , then runs along at  $E_1$  between the two flues, and, again returning, passes at  $E_2$  along the other side of the flue  $C_3$ . From this part of the air-flue, branches  $E_3$  pass off to each coking-chamber, and extend beneath the flue C to the fireplace B, with which they communicate through openings  $E_4$   $E_5$ .

Thus it will be seen that atmospheric air, entering the flue E at  $E_6$ , passes along the same in contact with the hot walls of both  $C_4$  and  $C_3$ , and lastly through  $E_2$ , whence it passes in a highly heated condition through the branch-flues  $E_3$  to the fireplaces of the several ovens, in order to enter there into combustion with the gaseous fuel employed, which, in some cases, may be kept ignited by a small fire of solid fuel on the grate shown at B. In E the air flows in the contrary direction to the current of the combustion-gases in  $C_4$ , and in  $E_1$  it flows in the contrary direction to that of the gases in  $C_3$ , so that the coldest air in each case comes into contact with the cooler part of the smoke-flues, and thus the heat is taken up by the air in the most effective manner. As the air in passing through the flue E  $E_1$  becomes heated to a considerable degree, in passing through the flue  $E_2$  (which is to a very slight extent in contact with the brickwork of the oven) it will not absorb any appreciable amount of heat therefrom, and even this absorption, small as it is, may be entirely avoided by arranging the flues so as

not to be in contact with the brickwork of the oven except where they enter it.

The hot air is made to enter the fireplace through the openings  $E_4$  and  $E_5$ , the latter being in close proximity to the inlet nozzle  $F$  for combustible gas, supplied through the pipe  $F_1$ ; while the opening  $E_4$  serves to supply air when required to the before-mentioned small fire on the grate. The hot-air flue is also by preference extended up in the front wall of the ovens, as indicated at  $E_7$ , in order to communicate at  $E_8$ , or at any other convenient point, with the upper part of the flue  $C_1$ , so that a portion of the hot air entering there may effect the combustion of any unconsumed combustible gases that may have passed away from the fireplace. The combustible gaseous constituents distilled off from the ovens escape through the flue  $G$ , and are led through proper pipes or hydraulic mains to any suitable apparatus for condensing the tar and removing from the gas other condensable and useful constituents; and the gas, after such purification, is then utilized in whole or in part as fuel for heating the coke-ovens, for which purpose it may either be led directly to the fireplace  $B$ , through the pipe  $F_1$  and nozzle  $F$ , or it may also be previously heated by first passing it through a pipe or flue situated within or close to the smoke-flues  $C_4$   $C_3$ . As, however, the quantity of gas consumed is small in proportion to the air-supply, the advantage gained in heating it is in most cases not sufficiently great to justify the additional expenditure and greater complication caused by providing apparatus for heating it.

As shown in Fig. 19, the combustion-gases may, before escaping up the chimneys,  $D$ , be made to pass through the flues,  $H$ , of steam-boilers or of ovens or kilns or evaporating-pans, in order still further to utilize their heat.

The patent also comprises another modification, in which there is only one external smoke-flue, into which the flues of all the ovens open, and on each side of which there is an air-flue so arranged that the external air passes in the contrary direction to the current of the combustion-gases. In a further modification, instead of having separate air-supply and smoke-flues, the same flues are made to serve alternately for taking up the heat from the combustion-gases and imparting such

heat to the air-supply, as in the well-known Siemen's recuperators (such as Hoffmann and Otto employ with the Coppée ovens).

The inventor lays special stress upon his arranging the recuperator-flues externally to the ovens, not inside them; since in the latter case too much heat is abstracted from the ovens, and their temperature is not so high as is desirable for the proper working of the coking-process.

From a paper by H. Simon<sup>1</sup> it appears that there were then (1885) at work three plants of Simon-Carvès ovens on the new system, comprising 50, 35, and 25 ovens respectively, all of them provided with recuperators. The ovens at Bear-Park are a foot longer than those at Crook, and take a charge of  $4\frac{1}{2}$  tons each, which requires rather more than 48 hours to work off, owing to irregularities over night and on Sundays. It is claimed that these ovens are much more substantial than those on the Coppée system, with their extremely thin walls, which are liable to burn away at the intense heat prevailing, whilst it is impossible to inspect them; also that it is most difficult to split up the current of hot gases equally all over the small flues of the Coppée system, and that the gases, rushing through the six-foot length of these vertical flues, have not time to part with their heat, whilst in the Carvès oven the gas has to run more than 100 ft. in one undivided current. Consequently the recuperators in the former system have much more work to do than in the latter. Lastly, it is urged that a continuous process of recuperation must yield more uniform results than one rising and falling with the change of regenerators. The coke from the new ovens fetches a higher price than any other coke for use in cupola furnaces; so far as blast-furnaces are concerned, there still seemed to be some prejudice in England which had been quite overcome in France, Germany, and Belgium.

The condensing-plant is of a very simple description, but as efficient as could be desired. An attempt to replace rotatory exhausters by Körting's injectors has failed.

From further notes, kindly supplied to the author directly by Mr Henry Simon, it appears that the *yield of coke* is about 77 per cent. in Durham, 69 per cent. in Accrington, 52 per cent. in Staffordshire. The *yield of ammonia*, expressed as

<sup>1</sup> *J. Iron and Steel Inst.*, No. 1, for 1885.

sulphate, is 1 per cent. to 1.25 per cent. with North-Country coal, and about 2 per cent. with Staffordshire coal. The *yield of tar* varies from 3 per cent. to 4 per cent., of about 1.1 specific gravity on the average, the quality being equal to any other high-temperature tar. The air is heated in the recuperator to about  $430^{\circ}$  to  $480^{\circ}$  C., and the temperature in the various flues is distributed somewhat as follows:—In the top flue C' (Figs. 16 and 17) it is  $1130^{\circ}$  to  $1180^{\circ}$ ; in the second flue (where more air is introduced),  $1260^{\circ}$  to  $1278^{\circ}$ ; in the third flue,  $1100^{\circ}$  to  $1120^{\circ}$ ; in the lowest side-flue,  $1125^{\circ}$  to  $1130^{\circ}$ ; in the flues C below the oven-sole,  $1540^{\circ}$  to  $1565^{\circ}$  C. Copper may be melted in the top flue, and iron will melt in the flue underneath the oven sole. Only best Dinas bricks can be employed in some of the flues, as the best obtainable material will alone resist such intense heat. The distribution of the heat is very even throughout the sides of each oven, so that the available coking-space is utilized to the fullest extent. The coal is put in nearly to the top of the arch and levelled evenly, even close to the doors; whilst in other ovens, which do not distribute the heat so well, a portion of the space close to the door is lost for carbonizing. It is claimed that, on account of the extreme simplicity of construction, the expense of erecting these ovens is very moderate, and their maintenance is also very inexpensive.

*Hüssener's Ovens.*—Another modification of Carvès ovens, equally provided with an air-heating apparatus, has been introduced into Germany by A. Hüssener (Ger. Ps. 16923 and 20196). Hüssener's ovens, of which 100 have been erected in Westphalia, are shown in Figs. 20 to 22. Their dimensions are: length 29 ft.  $6\frac{3}{8}$  in., width in the middle 1 ft.  $10\frac{5}{8}$  in., with a certain taper to facilitate the mechanical pushing out of the charge (as is usual in the case of all horizontal ovens, both those on the Coppée and on the Carvès system); height 5 ft.  $10\frac{7}{8}$  in. (the original Carvès ovens at Terre-Noire are 19 ft.  $8\frac{1}{4}$  in.  $\times$  2 ft.  $5\frac{5}{8}$  in.  $\times$  4 ft. 9 in.). Their available space is 88 per cent. of the total space, and they take a charge of  $5\frac{1}{2}$  tons of finely sifted, dry coking-coal. The charging takes place by four holes, *k k*; the ends are closed by doors turning on hinges; the discharging takes place by the ordinary pushing-out machine (ram). The end walls between the two ovens are strengthened by buttresses, *t*, which at the same time prevent

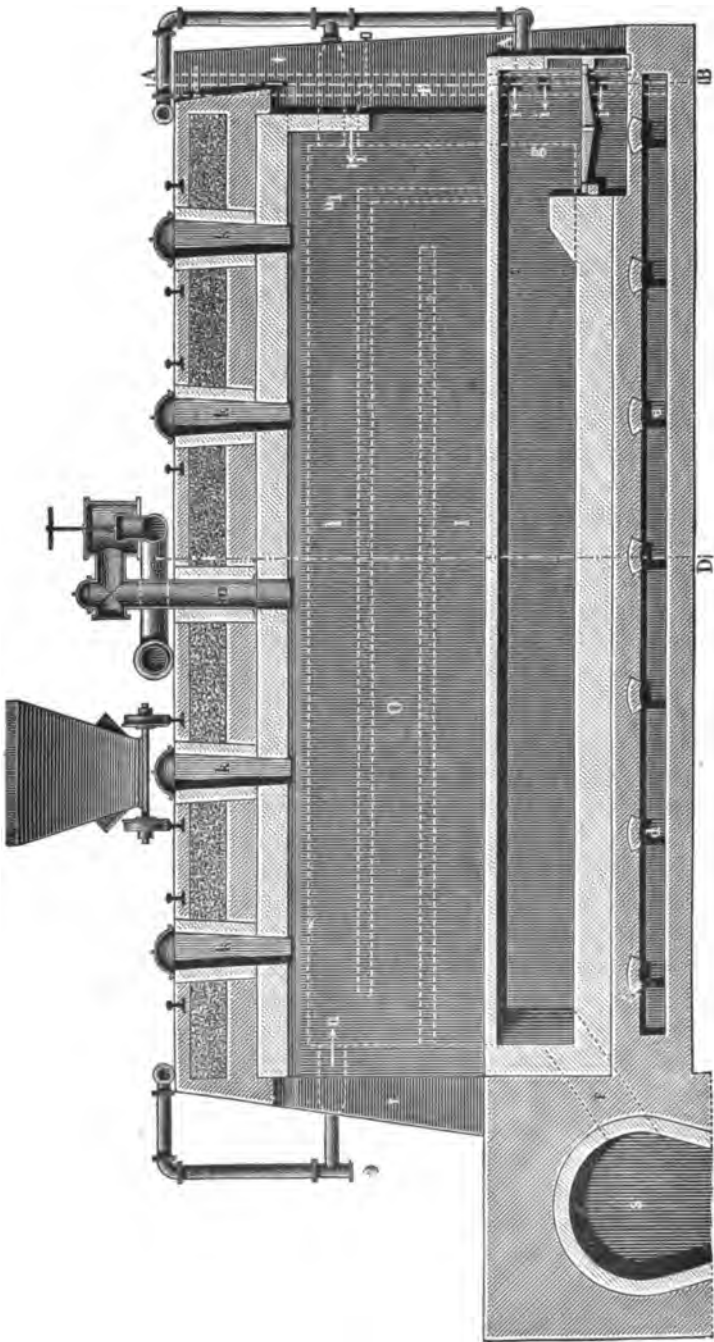


FIG. 20.

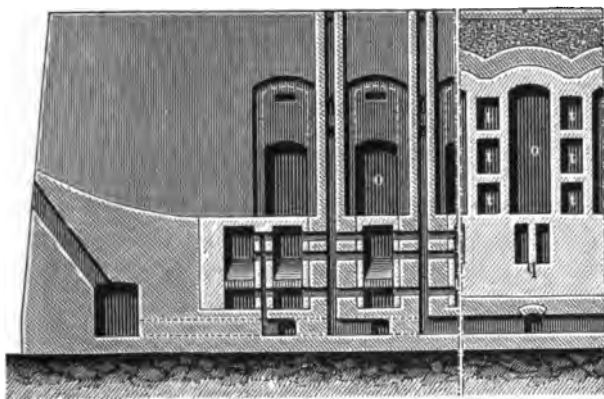


FIG. 21.

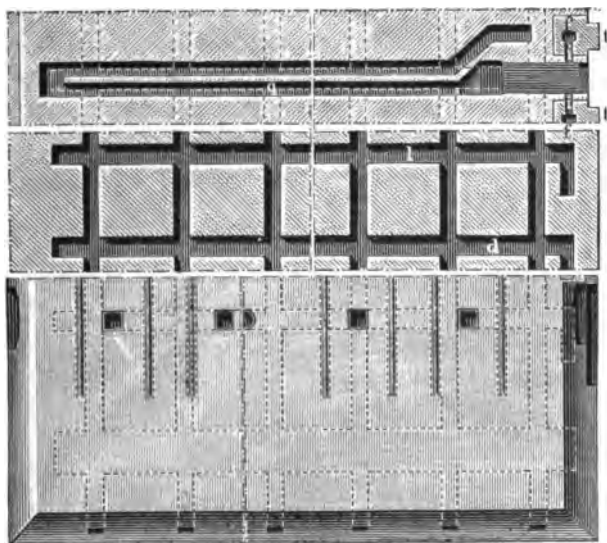


FIG. 22.



air from entering into the flues. The gases are aspirated by means of an exhauster through the outlet *m*, and are forced through the condensers and scrubbers: they then return to the ovens, and issue by the tube *A* over the fire-grate *g*, where they take fire. The fire-gases travel round the partition *q*, rise at one end up to the top flue *l*, and descend through the three horizontal flues *ll* and the snore-hole *r* into the main-flue *s*. The mouth of the gas-inlet pipe *A* is an annular double tube, like a Bunsen burner; whilst the inner tube conveys the air for combustion, the combustible gas issues through the annular space, and both enter at the same time into *g*. Owing to the distance which the products of combustion have to travel before they reach the main-flue *s* (about 100 ft. in a Carvès oven), they were formerly cooled down too much, and the ovens did not get hot enough, whilst the oven bottoms were fluxed. To avoid this, Hüssener introduced a previous heating of the air to about 300° C. in the flues *d e*; it is then conveyed through the small flue *f*, contained in the buttress *t*, partly through *i* in the grate-space *g*, partly through *i*<sub>1</sub> into the top flue *l*, and in both places gets mixed with gas. This does not seem to have met with complete success; but after adding further gas-inlets at *u* and *u*<sub>1</sub>, the fire on the grate *g* could be left out, the gases sufficing for heating the retorts. [It seems pretty evident that this sort of firing the ovens is not so economical as Otto's; this would also appear from the fact that the Otto ovens have a good deal of gas to spare.]

The cost of erecting a set of 100 Hüssener ovens in Gelsenkirchen (Westphalia), according to a published balance-sheet, was:—

For utensils . . .	Marks 2,689.33	
„ buildings . . .	113,225.38	
„ machinery and iron-		
work . . .	416,624.43	
„ railway . . .	38,193.48	
„ well and water-pond .	30,953.60	
	M. 601,686.22 = per oven,	M. 6016.86, or, say, £300.
„ coke-ovens . . .	326,475.51 =	3264.75 = £163
„ land . . .	105,655.15 =	1056.55 = £52
	M. 1,033,816.88 =	M. 10,338.16
	Or, say, £50,169; per oven,	about = £502.

The ovens are charged, at intervals of 60 hours, with  $5\frac{1}{2}$  tons of bituminous (proper coking-) coals (say, 700 tons per annum, or two-thirds of the output of the Otto ovens).

They are stated by Hüssener (*Stahl u. Eisen*, 1883, p. 405) to yield:—

	From Gas-coal.	From Coking-coal.
Large coke . . . .	61.70	75.00
Small coke . . . .	3.60	0.80
Coke-breeze . . . .	9.18	1.20
Tar . . . . .	2.72	2.77
Sulphate of ammonia . .	0.924	1.10

The ammoniacal liquor shows  $5^{\circ}$  Tw. and contains 1.65 per cent.  $\text{NH}_3$ . The tar is very thin; its specific gravity differs but little from that of the ammoniacal liquor. According to analysis made in November 1882, it yielded:—

58.83 per cent. distillate .	0.59 benzol $83-100^{\circ}$ C.
39.51 " pitch . . . .	0.49 " $100-140^{\circ}$ C.
1.66 " loss . . . .	0.39 solvent naphtha.
	1.37 pure phenol.
	0.95 pure anthracene.

The yield of phenol and anthracene is much higher than from ordinary gas-tar.

The *Semet-Solvay oven*, which is also an outcome of the Carvès principle, is extensively used, especially in Belgium and France. We give the following description of this oven, as erected in the Havré colliery near Mons (Belgium), according to communications from M. Demanet, manager.

The oven is 29 ft. 6 in. long, 5 ft. 7 in. high, 14.2 in. wide at one end, and 14.96 in. wide at the other (where the coke is pushed out). The heating-flues, where the gases are burnt, are built independently of the partitions between the ovens, and are therefore easily renewed without injury to the ovens themselves. They are formed of thin-walled, retort-shaped pieces (Fig. 25) fitted into each other by rebates, and thus joining tightly. This construction, whilst strong, admits of rapid transmission of the heat through the thin walls, and

Longitudinal Section.

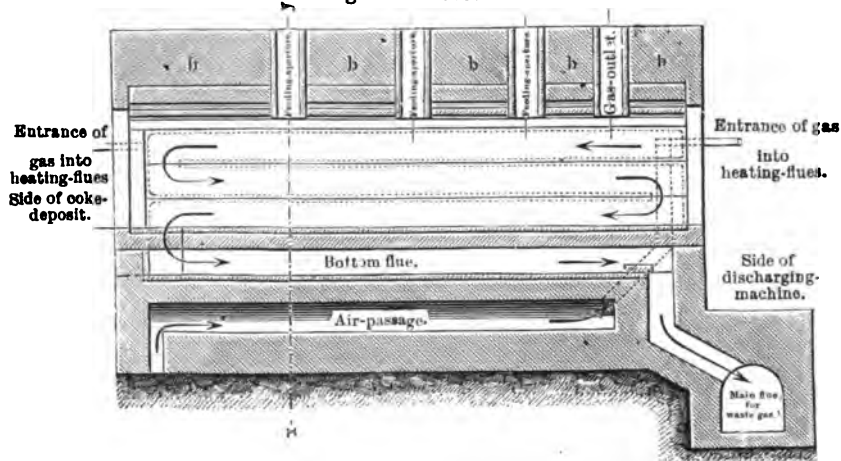


FIG. 23.

Cross-section x-y.

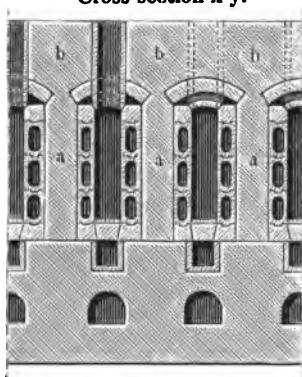


FIG. 24.



FIG. 25.

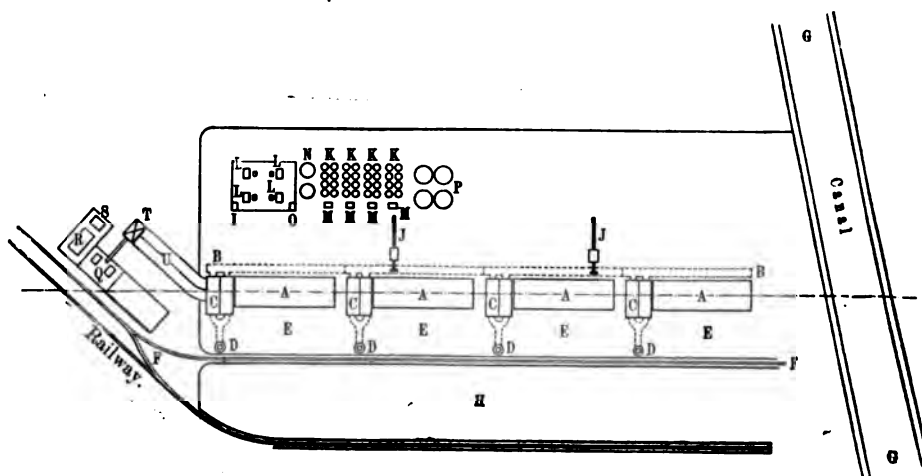


FIG 26.

thus quick work; and at the same time it reduces to a minimum the communication between the flue-gases and the vapours formed inside the ovens, which is very important for the yield of by-products.

Two forms of these retort-shaped flue-pieces are in use. One of these has three planes, the fourth being formed by the brick-work of the partitions; the other possesses four planes (Fig. 24), which is more expensive, but affords better protection for the partitions against the heat. Experience has not yet shown which is preferable. The partitions are made two bricks thick; the walls of the retort-shaped flues are only 2.36 to 2.75 in. thick.

In order to keep the heat together as much as possible, the top arches are 3 ft. 11 in. thick, and all cast iron doors are provided with sheet-iron outer doors.

Formerly small heating-flues were provided underneath the floors of the ovens, which were believed to be absolutely necessary for dry coals. Now, however, these are dispensed with, and the fire-gases are driven from the top downward, as shown in Fig. 25. A portion of these gases issues on that side of the ovens where the coke is discharged, and passes into the *upper* row of heating-flues, along the middle and bottom rows, and ultimately through the flue beneath the floor. A second supply of gas circulates on the opposite side of the oven into the *middle* row of flues. This arrangement avoids the formation of explosive mixtures and distributes the heat equally.

The air required for burning the gas is aspirated by a chimney, and is heated in a flue, situated below the hot oven-bottom, to 200° or 300°, before it issues into the heating-flue, where the gases are first introduced. This produces complete combustion and intense heat, and does away with the small fires formerly used for heating the oven-bottoms, so that at present only half the gases produced by the distillation of the coals are required for the coking-process, although the coal contains only 16 or 17 per cent. volatile constituents. The other half of the gases is utilized for steam-production, and the excess allowed to escape into the atmosphere. Much more steam is produced than the works can utilize, and the excess of steam is passed over to neighbouring ammonia and alkali works. We can to some

extent estimate the degree of utilization of the gases, when we consider that 4.5 per cent. water of the weight of coal and 1.5 per cent. tar is condensed, together 6 per cent., before the gas is passed into the heating-flues; thus leaving 10 or 11 per cent. for performing the coking process, only half of which is actually needed.

This utilization of gases is accomplished only by carefully preventing the entrance of air into the ovens. All doors are provided with asbestos-lined joints, and all the joints of the charging-holes, peep-holes, etc., are carefully faced, so that they close tightly by means of springs, and the luting with clay (always unreliable) is dispensed with. The air-tightness of the ovens is proved by the fact that the coke, when discharged, does not show any sign of combustion.

The gas is distributed in the heating-flues under uniform pressure by means of pipes of exactly the same section, so that all ovens receive an equal quantity of gas, and the draught from each oven into the main outlet-flue is also regulated by means of dampers, so as to be equal for all ovens. Hence the work can be regulated at one and the same time for all ovens by means of the chimney-damper. When entering the chimney, the temperature of the gas is scarcely 200° C.

At Havré four sets, A, of 25 ovens each (Fig. 26) are in use, every one of which consumes from 100 to 110 tons per day. The waste heat of the whole battery is passed, by subterranean flues, B B, underneath the steam-boilers C; the gas at last issues into the chimney D. Each set of ovens heat two steam-boilers of 800 superficial feet heating-surface. The chimneys are 82 ft. high and 5 ft. 3 in. wide.

E is the coke-pit made of cast-iron plates, situated above the railway F running to the canal G G. The coke is pushed out by means of the steam-ram I.

The gases and vapours produced in distilling the coal are aspirated by the exhausters L, and first cooled in tanks on the top of the ovens by means of cold water, so as to avoid any stoppage further on through the deposition of thick tar. They then pass through the condensers K and scrubbers M, and ultimately through tuyeres into the heating flues. Each set of 25 ovens is provided with a Beale exhauster, capable of aspirat-

ing 35,000 cubic metres per 24 hours, and adjustable for the process in each set.

The scrubbers M have each seven perforated sheet-iron shelves. N are tanks for ammoniacal liquor and tar; O is a pump connected with the reservoirs P, placed at such an elevation as to facilitate shipment into cistern-wagons.

The cost of an oven is 4600 fr., that of the condensing-plant 1600 fr. per oven; altogether, 6200 fr. per oven.

Each oven is charged with 4 tons of coal, which requires, on an average, 22 hours for distilling. A 25-oven battery finishes 25 charges per day. The yield is equal to that required theoretically, viz., with coal of 16 to 17 per cent. volatile constituents, 81 or 82 per cent. coke. As by-products are obtained 6 or 7 kg. sulphate of ammonia and 14 or 15 kg. tar per ton. Wages and repairs are slightly higher than without recovery of by-products—say 0.30 fr. per ton; but the wages do not exceed 1.30 fr. per ton, and as the profit on by-products is = 1.80 fr., the clear profit is 1.50 fr. per ton. Now an old coke-oven, without recovery-plant, costs 2000 fr., and produces 60 tons coke per month, or 3300 fr. for 100 tons per month; a Semet-Solvay plant for the same production costs 6200 fr., or 2900 fr. more. But the extra profit on these 100 tons being 150 fr. per month, or 1800 fr. per year, the additional outlay bears interest at the rate of 60 per cent. per annum.

At the Phoenix Iron Works at Laar (Rhenish Prussia)<sup>1</sup> each Semet-Solvay oven consumes 1643 tons of coal and yields 1273 tons coke per annum. The yield from 1000 kg. of dry coal is 775 kg. coke, 10 kg. tar, 7.6 sulphate of ammonia. The thick arch accumulates the heat, and admits of keeping the ovens hotter than any other system, so that, without recuperators or air-heaters, it is possible to mix from 73 to 77 parts of bituminous coal with 29 to 27 parts of dry coal and to obtain excellent coke, but of course less tar and ammonia than without the addition of dry coal.

We must not omit to mention that Hüssener does not admit these advantages of the Semet-Solvay ovens; but then we must

<sup>1</sup> *Chem. Ind.*, 1893, p. 338.

bear in mind that he is the inventor of a competing system (pp. 127 *et seq.*).

The following comparison of Semet-Solvay ovens in use at Syracuse, N.Y., and beehive-ovens, is quoted from *Stahl u. Eisen*, 1895, p. 1070:—

	Semet-Solvay.	Beehive.
Number of ovens . . . . .	12	12
Average time of coking . . . . . hours	20	51½
Number of ovens discharged in 24 hours . . . . .	14.4	5.5
Coal coked in 24 hours . . . . . kg.	71,688	27,760
Coke produced in 24 hours . . . . . kg.	57,669	17,327
Sulphate of ammonia produced in 24 hours, kg.	772	nil
Tar produced in 24 hours . . . . . kg.	2651	nil
Yield of coke per cent. . . . .	80.7	62.3
„ sulphate of ammonia . . . . .	1.075	nil
„ tar . . . . .	3.69	nil
Value of coke made in 24 hours (marks) . . . . .	402.70	120.08
„ sulphate of ammonia do. (do.) . . . . .	214.28	nil
„ tar do. (do.) . . . . .	122.72	nil
	<hr/> 740.00	<hr/> 120.08
Value of products from 1000 kg. coal . . . . .	61.65	10.00
Cost of each oven (marks) . . . . .	6400	1260
Duration „ (years) . . . . .	10	5
Quantity of coke made in each oven (kg.) . . . . .	17,638	2957
Cost of oven per 1000 kg. coke (mark) . . . . .	0.35	0.46

In 1899 there existed in Belgium 579, in Great Britain 370, in the United States 297, in France 155, in Germany 97, in Japan 16 Semet-Solvay ovens; altogether 1514, with an aggregate production of about 1,720,000 tons of coke (J. H. Darby, *Stahl u. Eisen*, 1899, p. 1055).

According to *Eng. and Min. J.*, 1899, p. 424, the Semet-Solvay ovens at an English colliery yielded from 100 tons of coal: 70 tons coke, 4½ tons tar, 1½ tons sulphate of ammonia—303 gall. crude benzol, and the equivalent of 13 tons steam. At the prices of that time the recovery of the by-products yielded a profit of 50 per cent. on the expense connected therewith.

A coke-oven of the upright type is that of R. Barlen (Ger. P.

183670) who claims that the by-products are better protected against decomposition than previously, and that the coking process goes on more quickly and uniformly. By means of a set of Bunsen burners the sides of the coking chambers are heated quite uniformly in the horizontal direction, but more and more strongly from the top downwards, the burners being arranged all over the side of the chambers from the top downwards, and the flues for the combustion-gases in the same way.

We now enumerate a number of recent patents for by-product coke-ovens:—

Kros, Fr. P. 391228.

Wright, B. P. 13292, of 1907.

Dillon de Micheroux, Ger. P. 104864.

F. Otto & Co., Ger. Ps. 105432, 106959, 171901, 171203.

Coppée, Fr. P. 290799.

Gewerkschaft König Ludwig, Fr. P. 289213.

Hilgenstock, B. P. 19757, of 1899.

Schniewindt, Belg. P. 143472.

Rigby, B. P. 20716, of 1901.

Holmes, B. P. 25493, of 1901.

Audouin, Aus. P., class 26, No. 9101.

Henz, Ger. P. 183823.

Tschudy, U.S. P. 1139088.

Russig, in *Chem. Zeit.*, 1901, 478, reports on new processes in the industry of coke.

Poetter & Co., of Dortmund, heat the coke-ovens from above in a special manner, to lessen the speed of the heating-gases and get more equalized results.

C. Schmidt and J. Chasseur, of Mülheim a. d. Ruhr, avoid the drawback of unequal suction from the various ovens of a set by means of a receiver, provided with subdivisions, luted by the tar, the aspiration taking place through side-channels in these divisions.

The Universal Fuel Company of Chicago surrounds the coking-chambers with a brick grating, which is heated to a white heat by the flame and produces a very uniform heating.



Koppers (U.S. P. 862976) cools the gases approximately to the dew-point of water, passes them through a separator where the tar floating as mist in the gases is withdrawn from them, superheats them again and condenses the ammonia in an acid bath, kept at a uniform concentration. Koppers' horizontal coke-ovens are about 30 feet long, and hold from 6 to 7 tons of coal, which is coked in 28 hours, or in case of ground coal in 34-35 hours. The gas escaping during the first 12 or 13 hours is collected separately, as it has the quality of illuminating gas, and is used for the lighting of the town Firminy. The gas given out later on is used for heating the ovens. The ammonia is washed out of the gas by means of sulphuric acid, by the process of Koppers. The first (illuminating) gas is compressed by means of a Roots' blower to  $1\frac{1}{2}$  atmospheres and conducted in cast-iron pipes to Firminy where it is purified from hydrogen sulphide in the old way.

Weissbein (Ger. P. 144148), Collin (Ger. Ps. 138622 and 144828), Cunow (Ger. P. 143307), describe other improvements in recovery coke-ovens (Fischer, *loc. cit.*, pp. 99 *et seq.*).

Picák (Aust. P. appl. A7292, 6th December 1906, *Chem. Zeit. Rep.*, 1908, p. 4) takes tar and ammonia out of the gases from the destructive distillation of coal, etc., by the liquid, kept in constant circulation between the scrubbers and the ammonia still, the latter being at the same time heated by these gases.

*Condensing Plant for Tar and Ammonia connected  
with Coke-ovens.*

Every plant for this purpose comprises a receiver, air and water-coolers, ammonia-washers, and aspirating-apparatus; mostly also tar-separators like that of Pelouze and Audouin, described *supra*, p. 58, or of Feld, and many others which we shall describe in the section treating of the recovery of ammonia from gases produced in the distillation of coal.

In this place we will only describe a few of the most important condensing-plants constructed for coke-oven gases.

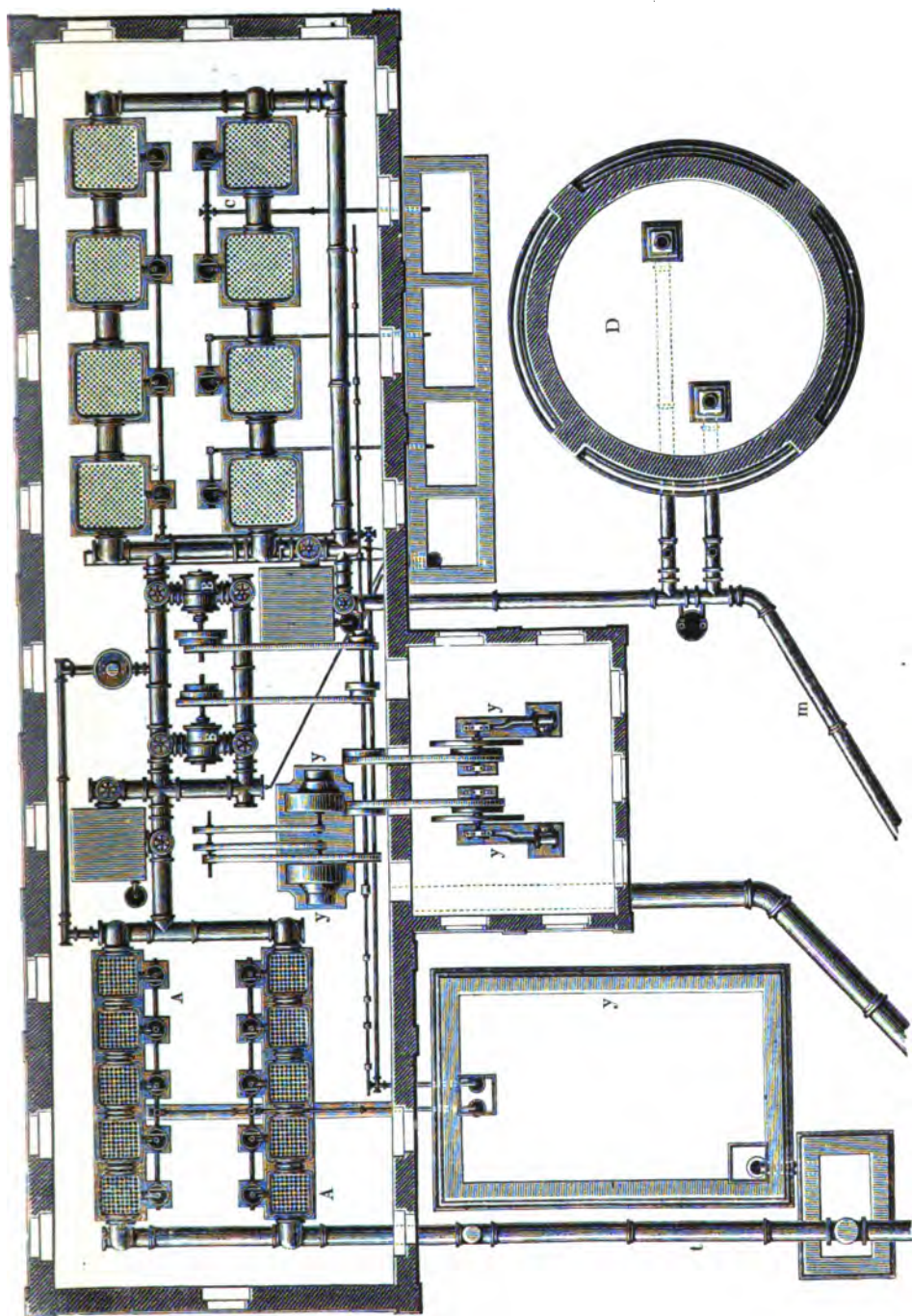


FIG. 27.

The *condensing-plant belonging to the Otto ovens* is shown in Fig. 27. The gas is first passed through the tube *t*, and cooled by upright wrought-iron cylinders or towers, A A. Within the cylinders are a number of iron tubes, fixed in partitions at top and bottom. The top partition forms a water-trough, constantly fed with cold water, which flows downward through the tubes into the bottom box, and thence away into the next tower. The towers are so connected that the cooling-water used in one of them is taken up to a second tower, and so on. The gas travels exactly in the opposite way in the space between the cooling pipes, entering at the bottom and issuing at the top, and is thus cooled. The temperature of the gas in the tubes rising from the ovens, is  $600^{\circ}$  to  $700^{\circ}$  C.; in the main receiver *L*,  $200^{\circ}$  to  $400^{\circ}$  (according to the distance from the tubes *i i*); in front of the gas-coolers,  $75^{\circ}$  to  $120^{\circ}$ ; after passing through them,  $17^{\circ}$  to  $30^{\circ}$ . In the coolers, A A, it loses a good deal of its tar and about 75 per cent. of its ammonia, in the shape of ammoniacal liquor. The quantity of cooling-water required is about 5 tons per oven in 24 hours.

The gas is aspirated from the coolers, A A, by means of blowers, B B, and is forced into the scrubbers, C C. These are upright wrought-iron cylinders or towers containing a large number of perforated iron shelves, 4 inches apart; water trickles down through these, whilst the gas travels from the bottom upwards. The ammonia is thus washed out; the liquor runs off at the bottom, and is, in case of need, pumped up over and over again, till it is strong enough for sale. Several scrubbers are connected in such a way that the gases at first passes through that containing the strongest liquor, and at last that fed with fresh water. Along with the remaining 25 per cent. of ammonia, the scrubbers also produce a good deal of tar. The temperature of the gas, which is now returned to the ovens, is  $13^{\circ}$  C. Since a large quantity of gas cannot be burned in the ovens, as it would produce too much heat (as mentioned above), the excess is stored in a gas-holder, D, and can be used for illuminating, for heating steam-boilers, or other purposes. The gas-holder also performs a very important part in equalizing the pressure, and in preventing any damage from chance explosions, in which case only water would be driven out from underneath the gas-holder.

The composition of this gas in a special case (the Pluto-pit ovens) was:—

	Molat. per cent. by vol.	Dry. per cent. by vol.
Benzene vapours, $C_6H_6$ . . .	0.60	0.61
Ethylene, $C_2H_4$ . . .	1.61	1.63
Sulphuretted hydrogen, $H_2S$ . . .	0.42	0.43
Carbon dioxide, $CO_2$ . . .	1.39	1.41
Carbon monoxide, $CO$ . . .	6.41	6.49
Hydrogen, $H$ . . .	52.69	53.32
Methane, $CH_4$ . . .	35.67	36.11
Water . . .	1.21	...
	<u>100.00</u>	<u>100.00</u>

Such gas has about half the illuminating power of ordinary, retort-made coal-gas, and can be used for lighting purposes by employing sufficiently large burners. In Westphalia it is employed for heating steam-boilers, along with the waste heat of the gases issuing from the recuperators into the chimney ( $420^\circ C.$ ).

A German patent of the firm C. Otto & Co. (No. 171203, of 1903, issued in 1905) prescribes conveying both all the tar and the ammoniacal liquor, beginning from a certain point back to the main receiver. The gaseous current thus established between the gases from the main and the condensater running back yields a product very rich in ammonia and benzol.

Further improvements are contained in the Ger. Ps. 203254 and 204570 of the same firm, and in their Ger. P. appl. O7014, of 1910.

According to their Ger. P. 174695 (of 1902, issued in 1906), the ammoniacal liquor obtained according to the preceding patent is cooled and then employed for washing the ammonia out of the gases.

A detailed description has been placed at my disposal by Mr Ernst Heuss, of Nied am Main, of a condensing plant attached to a set of Otto coke-ovens, which in 27 hours treat about 250 tons of coal, containing 10 per cent. of water. This plant consists of the following parts:—

- (a) 1 receiver at the ovens.
- (b) 2 air-coolers with tar-syphons.
- (c) 2 tubular water-coolers.

- (d) 2 high-pressure gas-exhausters.
- (e) 2 horizontal steam-engines.
- (f) 6 tar and ammoniacal-liquor pumps.
- (g) 4 centrifugal water-pumps.
- (h) 1 tar separator.
- (i) 1 tubular cooler for the last cooling of the gas.
- (k) 2 ammonia-scrubbers.
- (l) 1 water-separator.
- (m) 2 benzol-washers.
- (n) 1 separator for the washing oils.
- (o) 3 pumps for the same.
- (p) 1 flushing cooler for ammoniacal liquor.
- (q) 1 cooler for the heated cooling-water.

Tanks, pits, connecting pipes, shafting, etc.

The gas (about 2000 to 10,000 cub. ft. per ton of coal) leaves the ovens at the top through a rising pipe which, by means of a valve, dips into the semi-cylindrical iron receiver common to the whole set of ovens. The temperature of the gases on leaving the ovens is from 300° to 360° C., and it enters into the receiver with about 200° to 250° C. This reduction of temperature causes a condensation of the more highly boiling portions of the tar, together with most of the mechanically carried away coal-dust into "thick tar," a semi-fluid tar of low value, accompanied by a little thin tar and ammoniacal liquor containing mostly fixed ammonia salts. Some "thick tar" also accumulates in the pipes rising from the receiver and in the valves belonging thereto. In all these parts of the apparatus (in the receiver itself in distances of about 3 ft. from one another) cleaning-holes, easily closed by caps, must be provided, through which iron poles can be introduced for detaching the tar from the walls of the apparatus, and moving it forward to the "explosion-pit," connected with the main by a somewhat steeply inclined gas-pipe which descends into this pit and dips underneath the liquid. In this pit, made of brickwork and iron, the tar and ammoniacal liquor condensed up to this point are collected, and it serves at the same time as a safety factor; for in case of the gases in the main taking fire, no explosion can propagate itself into the subsequent parts of the condensing-plant, the gases getting vent in the "explosion-pit" by means of

an outlet-pipe, dipping into the tar and passing outside. In order to prevent such combustions and explosions as much as possible, the caps belonging to the cleaning-holes (*vide supra*) must be put on again immediately after use. The thin tar and ammoniacal liquor are run off the surface of the thick tar in the explosion-pit, and the thick tar is from time to time removed by means of iron rods.

It is not advisable to cool the gases too suddenly, as this gives rise to troubles through plugs of naphthalene forming in the pipes and valves.

From the explosion-pit the gases pass into the air-coolers *b*, where the remaining portions of thick tar are condensed, together with a good deal of thin tar and of ammoniacal liquor, and are removed by means of syphon traps. There are two air-coolers, in the shape of upright wrought-iron boxes, about 7 ft. wide, and 33 ft. high, with a partition in the middle not reaching quite to the top, so that the gases ascend in one half and descend in the other half, the inlets and outlets being both near the bottom. From here the gases pass into the tubular water-coolers *c*. These are perpendicular wrought-iron cylinders, 8 ft. diameter and 30 ft. high, with false bottoms into which wrought-iron pipes of 5 in. width are fitted. Through these pipes cold water is flowing; the gases are carried in the space between them, upwards and downwards, by means of partitions, in a current opposite to that of the cooling water. The liquids condensed during this passage pass through hydraulically-luted pots into the pit, where tar and weak ammoniacal liquor are collected. The hydraulic lutes must be made to correspond with the vacuum, produced by the exhausters *e*, placed at this point, which force the gases to the parts of the apparatus following behind them. The vacuum, beginning at the receiver *a*, naturally decreases later on, and thus varies from 0 to 200 mm., the pressure on the other side being from 300 to 250 mm. of mercury. Corresponding to this, the hydraulic seals must be at least 500 mm. deep.

On the other side of the pumps the gases are brought under a pressure of 250 to 300 mm. in order to drive them through the tar-separator, the after-cooler, the benzol- and ammonia-washers, back into the coke-ovens; on entering these the pressure should be still about 50 mm. This is

necessary in order to prevent explosions in the gas conduits, which must happen if there was a vacuum at this point at which air would enter into the gas conduits, instead of doing so only in the flues round the coke-ovens. Such explosions have sometimes taken place when new plants were being started, during which time consequently special care must be taken. Otherwise they may happen when the engine or the pump suddenly break down, or an accidental vacuum is caused by faults in the joints, etc. In such cases they can still be prevented by stopping the conduit in front of the ovens by means of a slide provided for that purpose.

The quantity of cooling-water should be regulated in such manner that it leaves the system at a temperature of  $70^{\circ}$  to  $80^{\circ}$ , the gases being cooled down ultimately to  $25^{\circ}$  to  $30^{\circ}$  C., but this is mostly attained only in the second cooler behind the pumps. The heated water is usually cooled down by flowing down over large surfaces and here meeting a current of air; it can be brought down to  $17^{\circ}$  or  $18^{\circ}$  and used over again for the water-coolers.

An exhauster forcing 100,000 cub. ft. of gas per hour against a total pressure of 3 ft. requires 17 or 18 h.p., with 80 revolutions per minute. They are now constructed up to pumping 300,000 ft. of gas per hour. Most coke-works require only three such pumps, two for actual work and a third as reserve in the case of a breakdown. The driving-engine, whether steam-engine or electromotor, should also be provided in duplicate. Of course pressure-gauges are provided in suitable places, as well as peep-holes and small taps for lighting the sample of gas issuing from them, the length of the flame (about 6 in.) and its vibrations serving as a good control for the working of the system.

All portions of the system must possess outlets for the condensed tar and liquor towards the great covered pit where these separate.

Behind the exhausters, *l*, we find first a tar separator, *h*, usually constructed on the principle of Pelouze and Audouin, as described on pp. 58 *et seq.*, viz., containing a series of perforated plates, the holes in each plate corresponding to a full place above and below, so that the gases are subjected to continuous shocks against solid surfaces, by which the foggy particles of tar are

united into larger drops, flowing downwards. Then comes a tubular water-fed cooler, *i*, by which the temperature of the gases should be brought down to 20° to 25° C. The cooling-water is brought back to 17° or 18° C. by means of the cooler *g*, which is a mass of thorns and works on the "graduating" principle.

The cooled gases now pass into the ammonia-scrubbers *R*, cylinders of from 7 to 13 ft. diameter and 25 to 50 ft. high, filled with a large number of wooden sieves, and fed with a well-distributed quantity of water. When leaving the second scrubber, the gas ought not to contain more than traces of  $\text{NH}_3$ , say, not above 5 g.  $\text{NH}_3$  to 100 cbm., but sometimes this goes down to 2 or 3 g. The liquor produced in the second scrubber, containing 4 to 6 g.  $\text{NH}_3$  per litre, comes up to 0.6 to 1.5 per cent.  $\text{NH}_3$ , and is used for feeding the first scrubber, where it comes up to the proper strength and is then sent to the ammonia works. The gases pass from the second absorber through the water-separator *l*, and then to the benzol condensers *m*, which are built exactly like the ammonia-washers, but fed with tar-oil (*cf.* p. 67), being equally followed by an oil-separator, *n*. Generally, about 85 to 90 per cent. of the benzol contained in the gases is recovered here. The residual gas now passes on to the coke-ovens, where it serves as fuel.

The yield of tar from good coking-coal averages  $2\frac{1}{2}$  to  $3\frac{1}{2}$  per cent., that of ammonia (calculated as sulphate) 1 per cent.

Improvements in the condensing-plant of by-product coke-ovens are described by Brunck (Ger. P. 137563), in order to recover the vapours formed during the drawing and charging of the ovens, where the principal gas-conductors are shut off by means of a special gas conduit (*Fischer's Jahresber.*, 1903, p. 17.)

#### *Quality of the Tar produced in various forms of Coke-ovens.*

We have already partially treated of this subject in connection with the gas industry, pp. 38 *et seq.* It has been extensively treated by Watson Smith, whose communications will be found in *J. Soc. Chem. Ind.*, 1883, pp. 403, 495; 1884, pp. 9, 64; and 1885, p. 451. We must refer for details



to those papers, and here give only a short abstract of their contents.

The tar or tar-oil from *Jameson's coke-ovens* (p. 99) has a specific gravity of 0.960 to 0.994. It contains no benzene, but very little toluene and rather more xylene. It mostly consists of oils boiling between 250° and 350° C., evidently belonging to the marsh-gas series; they are of little value for burning, and of but secondary value as lubricants. From the higher boiling-oils (up to the point at which pitch remains in the retort) a small quantity of paraffin, melting at 58°, separates. By treating the crude oils with caustic soda a fair amount of phenols is extracted; but they contain no carbolic acid, by far the largest proportion distilling between 235° and 300°, and they appear to resemble the complicated phenols found in wood-tar creosote. Neither naphthalene nor anthracene is present. Altogether the Jameson tar evidently belongs to the class of tars obtained by the distillation of coal at lower temperatures, and cannot be classed with the ordinary gas-tar. Watson Smith considers it an excellent material for creosoting timber. The results of Watson Smith entirely coincide with those obtained in 1873 by Behrens with the tar from Pauwels' coke-ovens.

H. E. Armstrong (*J. Soc. Chem. Ind.*, 1885, p. 451) expresses the opinion that the Jameson tar or oil might be improved by passing it through red-hot retorts, and is thus "intrinsically" more valuable than the tar from closed coke-ovens. This idea, as well as his opinion that the construction of the beehive or the Jameson ovens more nearly approaches the ideal of a coke-oven than the closed ovens of Carvès and others, is directly opposed to my opinion, and probably to that of most competent observers. Mr Watson Smith, who had already in 1883 conceived the plan of treating the Jameson oils as suggested by Armstrong, and who was on the point of patenting it, but relinquished this plan, states, as his reason for doing so, that the expense and losses of this process are ruinous unless these oils are to be had for almost nothing; and I entirely agree with that opinion.

A later analysis of another sample of Jameson tar by Watson Smith (*Industries*, 1886, p. 162) has in every way confirmed the conclusions formerly arrived at.

The tar from the *Simon-Carvès ovens* (p. 119), as produced from Pease's West coals, is black and thick, of specific gravity 1.106, and closely resembles the tar produced in the London gas-works, in containing very much naphthalene and anthracene, but less benzene, toluene, xylene, and carbolic acid than Lancashire tars. Paraffin is altogether absent. A fractional distillation of 2400 c.c. yielded :—

Below 120° . . .	6.2	per cent. by vol. water.
„ 120° . . .	1.6	„ „ naphtha.
„ 210° . . .	2.9	„ „ oil.
„ 220° . . .	1.3	„ „ „
„ 230° . . .	0.5	Nearly all solid naphthalene.
„ 300° . . .	18.6	{ Naphthalene and anthracene, mixed with intermediate oils.
Above 300° . . .	34.2	{ Nearly all solid crude anthracene ; little red oil.
Residue . . .	30.5	per cent. by weight half-coked pitch.

The pitch-coke was saturated with ammonia.

A determination of the real anthracene by Luck's method yielded 0.73 per cent., comparatively a very large amount, but if any considerable quantity of paraffin is contained in such tars (it was stated to be altogether absent in the above case ; see, however, below), this would make it useless for the manufacture of alizarine. The benzene seems to be very rich in thiophene.

An analysis of the Simon-Carvès tars from Pease's West, by S. A. Sadler, yielded 4.5 per cent. by volume of light oils, 20.4 per cent. by volume of creosote oils, with much naphthalene, and 34.2 per cent. of thick anthracene oil. Further treatment of the distillates gave :—

	Per cent. on tar.
Water . . . . .	10.00
Benzol, 50/90 per cent. . . . .	0.50
Solvent naphtha (90 per cent.) at 160° C. . . . .	0.60
Heavy naphthas . . . . .	0.40
Crude carbolic acid . . . . .	0.05
Creosote oils . . . . .	46.50
Anthracene . . . . .	0.74
Pitch and loss . . . . .	41.21
	<hr/> 100.00

From another set of Simon-Carvès ovens, erected at Bear-Park, and working with a different description of coal at a somewhat higher temperature, the following results were obtained (Watson Smith, *J. Iron and Steel Inst.*):—

	(a).	(b).	(c).
Ammoniacal water . . . .	...	...	7.44 per cent.
Light oils . . . .	5.12	5.12	6.28 "
Creosote oil . . . .	7.44	...	11.99 "
Naphthalene . . . .	...	...	10.17 "
Thick anthracene oil . .	34.03	...	...
Crude anthracene . . .	...	...	11.57 "
Naphtha . . . .	3.05	...	...
Pitch . . . .	45.17	...	57.29 "

Further treatment gave :—

50/90 per cent. benzol . .	0.703	...	per cent. on tar.
Benzol, boiling at 80° to 100°	...	0.53	" "
Toluol, " 100° to 120°	...	0.29	" "
Solvent naphtha, 90 per cent.	1.031	1.25	" "
Burning naphtha, 30 per cent.	0.434	0.20	" "
Carbolic acid (crude) . .	0.305	...	" "
Cresol (crude) . . . .	0.352	...	" "
Naphthalene (crude) . .	...	1.00	" "
Anthracene, 28 per cent. .	2.396	...	" "

Specific gravity of tar = 1.15. One ton of tar yielded 1.44 gall. of 50 per cent. benzol and 48.2 lb. of 28 per cent. anthracene.

The Bear-Park tar is seen to resemble normal retort-tar much more closely than the Pease's West tar; it contains much more benzol and carbolic acid than the latter (although less than the lowest average of carbolic acid from gas-retort tar, viz., 0.5 per cent.). It is rather less rich in naphthalene and anthracene, but still contains a great deal of those substances.

According to private information, received from Mr S. B. Boulton, the Simon-Carvès tar is sometimes very rich in paraffin, and this renders the anthracene made from it unsaleable, so that they have ceased making anthracene at their Bilbao works (*vide supra*).

An analysis of tar from *Otto-Hilgenstock ovens* has already been given (p. 116). Lunge and J. Schmid (*Chem. Ind.*, 1887, p. 337) have examined such tar—1st, from the "Germania" coke-

ovens, built on the Hoffmann-Otto principle, exactly as described in the text; 2nd, from the modified coke-ovens, built according to the Ger. P. 37280 (*cf.* p. 103), at the "Hibernia und Shamrock" pit, near Bochum (Westphalia). Analysis yielded the following results:—

	A. "Germania" tar.	B. "Hibernia" tar.
Spec. grav. at 15° . . .	1.1198	1.1368
Light oil up to 170° . . .	{ 6.55 p. c. weight = 7.43 p. c. vol.	{ 4.88 p. c. weight = 5.24 p. c. vol.
Middle oil up to 230° . . .	{ 10.54 p. c. weight = 10.16 p. c. vol.	{ 14.14 p. c. weight = 13.97 p. c. vol.
Creosote oil up to 270° . . .	{ 7.62 p. c. weight = 7.23 p. c. vol.	{ 9.99 p. c. weight = 9.77 p. c. vol.
Anthracene oil . . .	44.35 p. c. weight	22.65 p. c. weight
Pitch . . .	30.55 "	43.41 "
Water . . .	trace "	3.84 "
Loss . . .	0.39 "	1.09 "
	<u>100.00</u>	<u>100.00</u>

**Light Oil:—**

	"Germania" tar.	"Hibernia" tar.
Loss by chemical washing . . .	18.42 p. c. vol.	33.05 p. c. vol.
(including phenols) . . .	(3.80 " )	(5.32 " )
Distillate between 78° and 100° . . .	8.11 "	} 24.39 "
" " 100° and 140° . . .	17.56 "	
Spec. grav. of joint distillate at 15° . . .	0.869 "	0.862 "
Residue beyond 140° . . .	55.91 "	42.56 "

**Middle Oil:—**

Phenols (crude) . . .	26.0 "	37.66 "
Naphthalene (crude) . . .	43.30 p. c. weight	7.76 p. c. weight

**Creosote Oil:—**

Phenols . . .	11.0 p. c. vol.	18.33 p. c. vol.
Naphthalene (crude) . . .	43.6 p. c. weight	4.43 p. c. weight

**Anthracene Oil yielded crude an-**

thracene, percentage on tar . . .	4.13	0.93
Containing pure anthracene . . .	12.90	25.67

**Pitch:—**

Softening-point . . .	165°	160°
Containing fixed carbon . . .	51.56 p. c.	42.44 p. c.

The *distillate from the washed light oil* up to 140° could be nitrated without leaving any residue, and produced 133 per cent

weight of nitro-compounds of specific gravity 1.191, yielding only 1.1 per cent. up to 190°. It can therefore be regarded as consisting entirely of "aniline-benzol," in which a large quantity of xylene is certainly comprised. The portion boiling above 140° contained a considerable amount of naphthalene; but as this would be compensated by some naphtha, returned in the working of the middle oil, the whole of that portion may be called "heavy naphtha," without conducing to the expectation that all of it can be obtained in the state of commercial "solvent naphtha."

On rectifying the washed light oil from the "Hibernia" tar, the thermometer rose rapidly above 100°, then slowly to 140°. A considerable portion distils only above 170°. In the nitrification test 129.6 per cent. weight of nitro-compounds, specific gravity 1.188, was obtained. On distilling these compounds, there escaped between 110° and 190°, 2.47 per cent. of an oil which resisted further nitrification. Hence this "aniline-benzol" is not so pure as that from the Germania tar, and it, moreover, evidently contains very little benzene, but chiefly toluene and xylene. Its value is therefore much less than that of the benzol from the Germania tar. From the above results we can now deduce the following table of the products to be recovered from these two tars:—

	A. "Germania" tar.		B. "Hibernia" tar.	
Aniline-benzol . . . . .	...	1.68	...	1.12
Heavy naphtha . . . . .	...	3.64	...	2.06
Crude naphthalene from middle oil . . . . .	4.54	...	1.09	...
" " " creosote oil . . . . .	3.15	...	0.44	...
" " " total . . . . .	...	7.69	...	1.53
Crude phenols from light oil . . . . .	0.25	...	0.28	...
" " " middle oil . . . . .	1.56	...	4.90	...
" " " creosote oil . . . . .	0.42	...	1.75	...
" " " total . . . . .	...	2.23	...	6.93
Anthracene, calculated as commercial 33 per cent. . . . .	...	1.59	...	0.72
Creosote oil = middle oil + creosote, minus phenols and naphthalene . . . . .	...	8.24	...	15.67
Anthracene oil, filtered . . . . .	...	42.76	...	21.03
Pitch (very hard) . . . . .	...	30.55	...	43.41
Water . . . . .	...	...	...	3.84
		98.38		97.21

Light oil (boiling at 80° to 170°).	.	3·7 per cent.
Middle oil ( " 170° " 230°).	.	9·8 "
Heavy oil ( " 230° " 270°).	.	12·0 "
Anthracene oil (boiling above 270°)	.	4·3 "
Pitch . . . . .	.	67·0 "
Water . . . . .	.	2·3 "
Loss . . . . .	.	0·9 "
Spec. grav. . . . .	.	1·170

Spec. grav. at 19°, 1-106.  
1 kg. yielded up to 160°:—20 c.c. water.  
47 c.c. light oil.  
1 kg. yielded up to 240°:—188 c.c. middle oil.

	95°-100°	110°	120°	130°	140°	150°	160°	170°	180°	190°
per cent.	2	4	12	24	38	51	64	74	80	87

	182°-190°	200°	210°	220°	230°	240°
per cent.	5	18	42	62	76	85

Remy (*Z. angew. Chem.*, 1890, p. 327) obtained from such tar on the large scale 0.43 per cent. anthracene, 1.75 "aniline-benzol," 1.50 per cent. solvent naphtha, 34.00 creosote oil, 42.60 per cent. pitch, 8.10 per cent. water, 11.62 per cent. loss.

The tar from the Semet-Solvay coke-ovens at Glassport, Pa. (*cf.* p. 131), has the specific gravity 1.170, and yields:—

		Per cent.
Light oil, boiling-point	80° to 170° . . .	3.7
Middle oil, "	170° „ 230° . . .	9.8
Creosote oil, "	230° „ 270° . . .	12.0
Anthracene oil, "	over 270° . . .	4.3
Pitch . . . . .	. . . . .	67.0
Water . . . . .	. . . . .	2.3
Loss . . . . .	. . . . .	0.9

Complaints are sometimes made that coke-oven tar is of unequal quality, and on the average less rich in benzol than gas-tar. But this depends upon the quality of gas-tar taken for a standard. It must not be overlooked that coke-oven tar is always obtained from the same kind of coal, unmixed with shale, boghead, or other additions frequently made at the gas-works. There is absolutely no reason why tar from the same kind of coal, obtained in a coke-oven, should be of less uniform quality than gas-tar.

Composition of Westphalian coke-oven tar, as abstracted from Haarmann, pp. 15 and 16:—

	" Germania " pit.	" Pluto " pit.
Benzol for aniline . . .	1.68	0.10 to 0.30
Naphtha . . . . .	3.64	0.30 „ 0.90
Crude naphthalene . . .	7.69	5.20 „ 9.30
Crude phenols . . . . .	2.23	0.97 „ 1.41
Creosote oil . . . . .	8.24	8.50 „ 11.30
Anthracene oil . . . . .	42.76	22.00 „ 30.40
Anthracene . . . . .	1.59	0.71 „ 1.00
Pitch . . . . .	30.55	43.20 „ 48.30
Water . . . . .	...	1.20 „ 4.10

The *yield* of coke-oven tar from Westphalian coals is from 1.31 to 4.0 per cent., average 2.26. Saar coal yields about 4 per cent., Silesian coal even more. (With this we should compare the yields of tar in gas-works: Ruhr coal, 4.7 per cent.; Saar coal, 6.1 per cent.; Silesian coal, 5.1 per cent.)

Schniewindt (*Min. Ind.*, 1902, 152) gives the following com-

parison, illustrating the difference between coke-oven tar and gas-tar in working them up by distillation :—

Fractions.	Coke-oven tar.		Gas-tar.		
	Dominion coal.	Westphalian coal.	German.	American.	
				Good.	Bad.
	Per cent.	Per cent.			
Light oil . .	1.26	6.55	2.5	1.65	6.14
Middle oil . .	14.73	10.54	2.5	10.66	5.03
Heavy oil . .	7.07	7.62	25.0	8.18	7.50
Anthracene oil .	21.38	44.35	10.0	14.05	11.71
Pitch . .	53.03	30.55	60.0	61.16	68.25
Water . .	1.52	trace	...	1.81	...
Loss . .	1.01	0.39	...	2.48	1.37
	100.00	100.00	100.00	99.99	100.00
Free carbon . .	8.10	...	25	...	48.4
Spec. gravity . .	1.088	1.1198	1.155	...	1.255

A great number of similar statements on the products from various tars is made by Mallmann in *J. Gasbeleucht.*, 1905, p. 826, particularly with reference to the employment of the products in the manufacture of roofing-felt, of which we will give a short abstract. The tar from different gas-works is easily distilled; while some descriptions of tar are easily distilled, others show a strong inclination to boil over during the first period of the distillation, which is not merely due to their contents of water, but also that of "free carbon," which is much greater than that of normal tars. The pitch from bad tars is of much less value than that from normal tars, and the stills suffer much more by overheating in their case. Among roofing-felt makers there is a strong prejudice against coke-oven tars, but this is quite unfounded. Mallmann gives a long list of the yields of fractions from various tars; so do Rispler, in *Chem. Zeit.*, 1910, p. 51; Hooper, in *J. Gas Lighting*, 1911, p. 100; Jayne, in *J. Soc. Chem. Ind.*, 1911, p. 193.

Hubbard, in a Circular of the U.S. Office of Public Roads, 1912, gives analyses of 26 American coke-oven tars, together with statements of the temperature of the ovens and the yields. We abstain from quoting his figures, as there are no statements



concerning the origin and quality of the coals coked, so that no useful comparisons can be made.

J. M. Weiss (*J. Frankl. Inst.*, 1911, pp. 277 *et seq.*) also makes statements concerning American tars. He found :

	Free Carbon.	Spec. grav. at 15.5° C.
Gas tar . . .	from 16.67 to 33.17 per cent.	1.203 to 1.296
Coke-oven tar . . .	4.04 „ 19.06 „	1.178 „ 2.258
Water-gas tar . . .	1.04 „ 1.08 „	1.078 „ 1.090

Generally the specific gravity of the tars increases with their percentage of free carbon. It is remarkable that in some American coke-oven tars there is as much free carbon as in normal gas-tar.

*General Conclusions.*—As an outcome of all we know on the subject, we may draw the following inferences:—Closed coke-ovens of the modified Coppée type (Hoffmann-Otto's system) yield a description of tar at least equal in value to ordinary gas-tar. The "benzol" contains a large proportion of real benzene, and is practically free from non-nitrifiable products. There is a good deal of heavy naphtha. The quantities of phenol, naphthalene, and anthracene are normal. Unlike gas-tar, the tar from these ovens contains much less creosote oil and hard pitch than anthracene oil, which is rather an advantage than otherwise. All this is easily understood, since these ovens work at least at the same heat as gas-retorts.

Ovens of the beehive class, modified by applying to them *external* heating-flues and recuperators, which work at a lower temperature than those just mentioned, yield a somewhat inferior tar. The "benzol" contains very little benzene and a notable proportion of non-nitrifiable products. There is also less naphtha and much less anthracene. Moreover, it is very difficult to dehydrate. The very small proportion of naphthalene and the large proportion of phenols it contains is very noteworthy. Still this tar must be classed with gas-tar and worked up in the same way; it is entirely distinct from other tars, obtained from internally heated beehive coke-ovens of the Jameson type (p. 99).

The suggestion has been made (as mentioned in Mr Weldon's presidential address, *J. Soc. Chem. Ind.*, 1883, p. 8) that alkali-makers and other manufacturers whose establish-

ments are situated in coal-districts, instead of feeding their furnaces with coal in the usual manner, should become coke-producers—the coke-oven gas, along with the coke, to be their fuel, whilst the tar (or oil) and ammonia were to pay for the small coal or “duff” to be employed. Thus they would get their fuel virtually for nothing. Splendid as this conception is, a calm consideration of the facts at once shows that it is impracticable, most certainly with the Jameson process, which Weldon had in view. Whether it is more practicable, when so employed, to convert all the coal at once into “producer-gas,” with recovery of the by-products, we shall see later on. I. Levinstein (*op. loco*, p. 217) believes that the suggestion mentioned by Weldon would be practicable for any manufacturer consuming at least 300 tons of coal per week, and subjecting the gas to the action of a fatty absorbent in order to recover the benzol. Levinstein holds that the coke and the gas will be practically equivalent in heating-power to the coal carbonized; but this evidently cannot be the case, since the tar is taken out and all the heat imparted to the gases in the coke-oven must be lost in cooling the gases for the recovery of the by-products. Scheurer-Kestner (*Comptes rend.*, vol. xcvi., p. 179) calculates the loss of calorific power in transforming coal into coke and gas at 19.3 per cent., and holds Weldon’s proposal to be quite impracticable.

*Extraction of Benzol, etc., from Coke-oven Gases.*

The extraction of benzol from coke-oven gases has been treated *supra*, pp. 70 *et seq.*, in connection with that extraction from illuminating gas. We shall in this place, however, give some statements on the actual development of that industry. According to Kraemer (*Glückauf*, 1897, p. 179), the German production of benzol from gas-tar in the eighth decade of the last century was only 1200 tons per annum; nothing from coke-oven tar. About the year 1900 it was estimated at 4000 to 5000 tons; 1896 at 7000 tons, viz., 4000 tons from coke-oven gases and 3000 tons from gas-tar and coke-oven tar. In 1901 the production of benzol was estimated by Brunck at 25,000 to 30,000 tons, by Frank at 28,000 tons. For 1904 Haarman puts the total production at 36,000 to 38,000 tons; Rau at 40,000

tons, viz., 2000 from gas-tar, 4000 from coke-oven tar, and 34,000 from coke-oven gases. In 1908 the German production had risen to 90,000 tons, of which 80,000 tons came from coke-oven gases, and 10,000 from gas-tar and coke-tar.

Grebel (*Petroleum*, 1908, p. 1191) estimates the production of benzol in the year 1907—

In Germany, at	.	.	.	.	60,000 tons
„ Great Britain	.	.	.	.	25,000 „
„ France	.	.	.	.	8,000 „
„ Belgium	.	.	.	.	6,000 „

For 1911 Köhler estimates the quantity of benzol producible in Germany from the 24 million tons of coal coked at “rationally” worked places at 130,000 tons; if all coke was made with recovery of all products, the German production might be driven up to 160,000 tons. Of course nothing like that quantity could be sold. The yearly sales of the German Benzol Association were (tons)—

	1906.	1907.
To colour-works	23,663	29,637
„ gas-works	1,487	1,240
For other purposes	6,121	10,511
Total	31,271	41,388

The same Association in 1909 made 45,000 tons of benzol, toluol, xylol, and solvent naphtha; for 1910 it estimated the possible production of benzol at 85,000 tons, of benzol homologues at 15,000 tons. The sales in this year were 56,000 tons benzol and 6800 tons homologues. The actual quantities delivered were, in 1910: to colour-works, 32,300 tons; to gas-works, 928 tons; for gas-motors, 33,322 tons; for other purposes, 1240 tons. It should be noted that the sales of benzol for motors exceeded those to colour-works.

In the year 1912 Germany exported 24,712 tons; in 1913, 34,032 tons benzol.

According to Bakerfield (*Chem. Trade J.*, 1915, p. 595), if all the coke-oven gases in the United Kingdom were treated for the recovery of benzol, this would produce 60 million tons benzol, and another 12 million tons might have been produced by debenzolizing the illuminating-gas at the gas-works.

For the United States, Puning (*J. Gas Lighting*, 1915, p. 84) states that if the benzol were recovered from all the coal carbonized in the States in by-product coke-ovens, the annual production would be 29,600,000 gall., valued at \$4,400,000.

According to *Chem. Ind.*, 1915, p. 168, a number of large installations for the production of benzol, etc., from coke-oven gases were in course of erection in the United States and Canada. Among these we mention that erected by the Otto Coking Co. for the Lackawanna Steel Co. which was started in June 1915, producing daily from 1500 to 2000 gall. light oils; all the benzene and toluene producible having been sold beforehand at prices leaving a large profit.

From the *Asphalt- und Teerindustrie Zeitung*, 1910, pp. 639 and 679, we take the following notes on the development of the benzol production and the requirements of benzol in France. Up to 1896 the production of benzol in that country was only a few hundred tons per annum. In 1896 and 1897 a few coke-works in the north of France started the recovery of by-products, and further works followed in 1901. At present (in 1910) the French production of benzol is about 13,008 tons, but the demand for it has largely increased, owing to the development of the motor cars, to 50,000 tons, which are covered by importation from Germany, England, and Belgium.

#### *Recovery of Ethylene from Coke-oven Gases.*

Fritzsche (*J. Soc. Chem. Ind.*, 1898, 27) has proposed to recover from coke-oven gases, before burning them, not merely the benzol hydrocarbons, but also *ethylene*, by means of scrubbing them with strong (96 per cent.) sulphuric acid (after removing the benzene hydrocarbons,  $H_2S$  and moisture) in the shape of ethyl-sulphuric acid. When heating this, *ethylic alcohol* is set free, which contains no essential proportion of propylic or isopropylic alcohol or of other impurities. In this manner 26 g. absolute alcohol was recovered from 1 cbm. of coke-oven gas, but this requires a very large apparatus, as he concludes from his laboratory experiments, viz., 12.5 cbm. per 1 cbm. gas produced per minute, when employing a pressure

of 4 atmospheres; nor could the difficulties be lessened by working at an essentially higher pressure. Klar (*Z. angew. Chem.*, 1899, 588) judges very favourably of this proposal, which would yield many million gallons of alcohol, and this, as he thinks, at a comparatively low figure; but it does not appear that Fritzsche's process has ever been tried on a working scale, perhaps just because it was *not* protected by a patent.

*Illuminating-gas from Coke-ovens.*

Recently, important utterances have been made in favour of giving up the gas-retort system altogether in favour of coke-ovens of the most improved type, recovering all the by-products and yielding gas which can be enriched to any suitable extent by the benzol recovered from the same coal, or else used as it is in lamps provided with incandescent mantles. This question has been discussed at length in a paper by F. C. Moon (*The Gas World*, 15th September 1906, pp. 512 *et seq.*), giving an account of a discussion before the Institution of Gas Engineers, raised by Thomas Glover, of which we shall now give a short abstract. The former prejudice in favour of beehive coke for metallurgical operations has at length been vanquished, and it is recognised that coke of the best quality can be produced in conjunction with the recovery of by-products; that the quantity of coke per ton of coal is higher; and that the value of the by-products is considerably in excess of the increased cost for wages, repairs, and interest charges. At present the residual gas from by-product coke-ovens is usually deprived of part of its luminosity by taking out the liquid hydrocarbons, but it is quite unnecessary to do so, and the surplus of gas left after heating the ovens is rarely made use of. On the other hand, the time seems to have come when the matter should be started from the other end; that is, the gas-works should produce metallurgical coke and by-products, and use the rich gas for illumination and the poor gas for heating the ovens, etc. The Simon-Carvès Company estimates the capital cost for this purpose at £120 per ton of coal, including everything from the coal brought to the ovens to the outturn of the coke, tar, sulphate of ammonia, and benzol. For a smaller installation at a gas-works it is safe to allow £150 per ton of coal carbonized

per diem, and another £20 for purifying and measuring the gas, and for duplicate hydraulic mains and valves for separating the rich and poor gas. This £170 has to be compared to the corresponding items in ordinary gas-works = £300. The difference in favour of coke-ovens is £130 per diem = 13s. per ton per annum of 200 days. Allowing interest at the rate of 5 per cent., the interest charges for coke-oven plant would be 7s. 8d. per ton of coal carbonized less than for coal-gas manufacture. The products would be: 10,500 cub. ft. of gas, of which 4000 cub. ft. is available for sale, of an illuminating power certainly not below 16 candles; 8 gall. of tar, rather inferior in quality to that from gas-works; 25 lb. sulphate of ammonia, and 1½ gall. of benzol, extracted from the gas used for heating the ovens.

The working costs (assuming them over 33 per cent. in excess of what is stated by a competent authority) are 1s. 8d. per ton of coke. Repairs and depreciation, allowing 7½ per cent. on the total cost, on the basis of 200 working days, amount to 1s. 3d. per ton of coal carbonized, which compares with 2s. 3d. for coal-gas plant. If operating wages are taken at 1s. 8d. per ton of coke, equivalent with 1s. 2d. per ton of coal, the total charges for wages, repairs, and depreciation amount to 2s. 5d. per ton of coal carbonized.

On this basis the following comparison is made between the results of existing gas-works and those to be anticipated from the installation of coke-ovens. Two such tables are given, one for the Newcastle-on-Tyne gas-works, the other for the South Metropolitan gas-works, on published data, taking the price of metallurgical coke at 16s. 8d. at Newcastle, and 20s. in London.

#### NEWCASTLE-ON-TYNE, 1905.

##### *Cost per ton of Coal carbonised at Gas-works :—*

	s.	d.		s.	d.
Coal. . . .	8	6.21	Coke, <i>less</i> labour . .	4	4.98
Wages . . . .	2	5.40	Tar . . . . .	0	9.47
Purifying . . . .	0	8.20	Ammonium sulphate	1	6.75
Maintenance . . . .	2	0.61	10,080 cub. ft. of gas		
Salaries . . . .	0	4.20	at 8d. per 1000 . .	7	3.42
	<u>14</u>	<u>0.62</u>		<u>14</u>	<u>0.62</u>

*At Coke-oven plant:—*

	s.	d.		s.	d.
Coal . . . . .	8	6.21	Gas, 4000 cub. ft. at 8d. . . . .	2	8.00
Purifying 400 cub. ft. . . . .	0	3.00	Tar, 8 gall. at 1d. . . . .	0	8.00
Salaries . . . . .	0	4.20	Ammonium sulphate, 25 lb. at £12, less cost of materials . . . . .	2	1.00
Wages, incl. purifying, etc. . . . .	1	2.00	Benzol, 1½ gall. at 9d. . . . .	1	1.50
Repairs and depreciation . . . . .	1	3.00	Coke, 14 cwt. at 10d. . . . .	11	8.00
	<u>11</u>	<u>6.41</u>		<u>18</u>	<u>2.50</u>
				<u>11</u>	<u>6.41</u>
				6	8.09
Credit, less interest charges . . . . .				0	7.80
Additional profit per ton of coal carbonized . . . . .				<u>7</u>	<u>3.89</u>

## SOUTH METROPOLITAN GAS COMPANY.

	s.	d.		s.	d.
Coal . . . . .	11	0.12	Coke, less labour . . . . .	5	3.85
Wages . . . . .	2	0.58	Tar . . . . .	1	2.38
Purifying . . . . .	0	8.67	Ammonia . . . . .	2	0.79
Maintenance . . . . .	3	4.19	10,733 cub. ft. of gas at 10½d. per 1000 ft. . . . .	8	11.33
Salaries . . . . .	0	4.79		<u>17</u>	<u>6.35</u>
	<u>17</u>	<u>6.35</u>			

*Coke-oven plant:—*

	s.	d.		s.	d.
Coal . . . . .	11	0.12	Gas, 4000 ft. at 10½d. . . . .	3	5.00
Purifying 4000 ft. . . . .	0	3.10	Tar, 8 gall. at 1d. . . . .	0	8.00
Salaries . . . . .	0	4.79	Ammonia . . . . .	2	1.00
Wages (as above) . . . . .	1	2.00	Benzol . . . . .	1	1.50
Repairs and depreciation . . . . .	1	3.00	Coke, 14 cwt. at 1s. . . . .	14	0.00
	<u>14</u>	<u>1.01</u>		<u>21</u>	<u>3.50</u>
				<u>14</u>	<u>1.01</u>
				7	2.49
Credit, less interest charges . . . . .				0	7.80
Additional profit per ton of coal carbonized . . . . .				<u>7</u>	<u>10.29</u>

On discussing the question whether it would be profitable to reserve for sale the whole of the oven gas, and employing producer gas for raising the necessary heat, it is shown in the paper, on the hand of figures, that no financial gain can be expected beyond that shown by ovens of the type in ordinary use, but a middle course might be adopted, about which we must refer to the original, as no experience exists for guidance up to the present.

Not all the recent public utterances are in favour of substituting coke-ovens for the gas-retorts. Thus Bury (*J. Gas Lighting*, 1907, p. 962) estimates the surplus gas available from good coke-ovens at only one-third of the whole. Schlicht (*ibid.*, p. 974), considers the question, which pays better—a gas-works of the old type, or a system of coke-ovens of the most recent type—as not yet decided.

Herbst mentions the case of the gas-works at Boston, where the gas passing over during the first half of the carbonating-process (44·5 per cent.) is used for illuminating purposes, that of the second half (50·5 per cent.) for heating the ovens. A similar fractionation has been practised at Mülheim and at Essen. Several places in Germany receive such gases from a considerable distance, as Homberg, Essen, Mülheim.

Schreiber (*Entw. d. Kokereiindustrie Niederschlesiens*, 1911, p. 51) also strongly recommends the recovery of illuminating gas from by-product coke-ovens.

*Statistics on the Recovery of Tar and Ammonia from Coke-ovens.*

We shall in the first instance quote the figures given by Haarman (*loc. cit.*, pp. 7 *et seq.*) on the *total production of coke*, some of them rounded off to entire millions. He states the productions for the years 1900 to 1902 as follows:—

	1900.	1901.	1902.
	Tons.	Tons.	Tons.
Germany . . . .	14,952,947	13,839,357	14,004,398
Great Britain . . . .	10,000,000	9,500,000	10,000,000
Belgium . . . . .	2,434,678	1,885,000	2,048,070
Russia . . . . .	2,250,000	1,993,000	2,000,000
France . . . . .	2,289,102	1,850,000	1,850,000
Austria-Hungary . . . .	1,238,000	1,332,000	1,300,000
Spain . . . . .	350,370	455,586	404,503
Sweden . . . . .	9,005	60,000	60,000
Denmark . . . . .	16,500	16,500	18,800
Italy . . . . .	26,000	26,000	28,000
Total for Europe . . . .	33,566,602	30,957,443	31,713,771
Japan . . . . .	30,000	84,680	70,000
Australia . . . . .	126,213	128,882	126,872
United States . . . . .	17,701,713	19,606,206	23,039,367
Canada . . . . .	157,134	379,600	342,392
Total for the world . . . .	51,581,662	51,247,811	55,292,402



We now come to the *coke-ovens built on the recovery plan*. In Germany up to 1890 most ovens were still built on the open plan. Between 1891 and 1895, already 30 per cent. of the newly erected ovens were on the recovery plan; between 1896 and 1900, 62 per cent.; from 1901 to 1903, upwards of 75 per cent.; and since 1904 no open ovens whatever have been built. In 1904 there were in Germany altogether 19,309 coke-ovens, of which 9110, or 47·2 per cent., were on the recovery plan, but these produce much more coke than the open ovens; in that year about 9,750,000 tons of coke (=57·4 per cent.) were made in the recovery ovens, against 7,280,000 tons (=42·6 per cent.) in open ovens.

In 1904 the quantity of tar produced in German coke-works was 276,805 tons, that of the gas-works only about 225,000 tons—that is, considerably less. The importation of tar from foreign countries was 40,641 tons; the exportation from Germany, 32,872 tons. The importation also comprised considerable quantities of tar-products, viz., light oils, heavy oils, carbolic acid, naphthalene (12,444 tons), anthracene (1230 tons), and pitch, mostly from Great Britain.

The quantity of ammonia turned out by the German coke-ovens, calculated as sulphate, amounted to—

71,118 tons in 1902
80,979     "     1903
100,212    "     1904

(More about this in Part II.).

In the west of Germany in 1904, a number of coal companies combined to erect a tar distillery for treating their coke-oven tar, under the style of Gesellschaft für Teerverwertung, at Meiderich, near Ruhrort. This enormous factory was begun in May 1905, and started work in February 1906. Already, in 1906, 96,000 tons of tar were distilled; in 1907, 129,400 tons; in 1908, 160,000 tons were treated. Apart from the tar, considerable quantities of light oils (crude benzol) were treated, as they are recovered from the coking-gas by washing with heavy oils (pp. 70 and 155); in 1907, 10,000 tons of commercial benzol were got from this source. Of pure naphthalene, solidifying at 79°·6 C., 5000 tons were made, also a large quantity of 40 per cent. anthracene. The distillation takes place in intermittently

working stills like those shown in Chapter V. The yields are, from 100 tar: 58 pitch, 30 heavy oils of specific gravity above 1.0, 0.7 crude benzol, 5 pure naphthalene, 0.55 pure 40 per cent. anthracene, 0.05 pyridines for denaturing alcohol, 0.4 phenols calculated as pure phenol. The percentage of water in the tar worked averaged 4 per cent. (communicated to the author by the manager Dr Spilker).

The yield of tar per cent. of the coal must needs be smaller in by-product coke-ovens than in gas-works, since the latter work a more strongly bituminous coal. Westphalian coking coal yields from 1.3 to 4, average 2.26 per cent.; Saar coal, 3.9 to 4 per cent.; Silesian coal still more.

Haarmann (*J. Gasbeleucht*, 1906, p. 753) describes in detail the industry of by-products from coal, more especially in Germany. The development of this can be best seen from the figures showing the number of coke-ovens built by the firm of C. Otto & Co., of Dahlhausen, which is quite at the head in this line. They erected:—

	Ovens without recovery of by-products.	With recovery of by-products.
In 1881 to 1885 . . .	2144	350
„ 1885 „ 1890 . . .	1886	845
„ 1891 „ 1895 . . .	1371	913
„ 1896 „ 1900 . . .	1206	1981
„ 1900 „ 1903 . . .	638	1940
„ 1904 „ 1905 . . .	none	1809
	<hr/> 7245	<hr/> 7838

We can see how the by-product ovens gradually came to the front, until in the last period they have become the only type adopted by the industry for new erections.

At the end of 1904, 47.2 per cent. of the coke-ovens in Germany were on the by-product recovery system. Since the output of these is about 50 per cent. higher than that of the open ovens, we may take it that of the 17 million tons of coke produced in Germany in 1904,  $9\frac{1}{2}$  millions, = 57.4 per cent., were made in recovery ovens, and  $7\frac{1}{2}$  millions, = 42.6 per cent., in open ovens.

The following figures are taken from the official statistics of

the German coke industry, published in No. 174 of the *Nachr. f. Handel u. Ind.*, 1911.

Districts.	1909.		1910.	
	Recovering by-products.	Not recovering.	Recovering by-products.	Not recovering.
Number of coke-ovens in—				
Rhineland-Westphalia . . . . .	13,785	5,365	14,932	5,190
The Saar district . . . . .	782	1,363	897	1,258
Lower Silesia . . . . .	750	160	790	160
Upper Silesia . . . . .	2,244	18	2,264	18
Saxony-Thuringia . . . . .	...	207	...	195
Altogether . . . . .	17,561	7,113	18,883	6,821
Average number of ovens actu- ally at work . . . . .	15,416	4,490	16,333	4,602
Out of work . . . . .	2,145	2,623	2,550	2,219
Quantity of coal coked—	Tons.		Tons.	
German . . . . .	31,713,020		34,558,696	
Foreign . . . . .	266,577		248,436	
Altogether . . . . .	31,979,597		34,807,132	
	Coke.		Tar.	
	1909.	1910.	1909.	1910.
Annual production in—	Tons.	Tons.	Tons.	Tons.
Rhineland-Westphalia . . . . .	19,648,581	21,635,180	562,929	630,465
The Saar district . . . . .	1,440,748	1,513,835	38,901	41,195
Lower Silesia . . . . .	836,715	851,451	26,154	27,638
Upper Silesia . . . . .	1,594,408	1,640,152	118,837	123,319
Saxony-Thuringia . . . . .	66,160	65,432	...	...
Altogether . . . . .	23,586,612	25,706,050	746,821	822,617
	Benzols.		Sulphate of Ammonia.	
	1909.	1910.	1909.	1910.
Annual production in—	Tons.	Tons.	Tons.	Tons.
Rhineland-Westphalia . . . . .	41,249	64,877	237,950	268,318
The Saar district . . . . .	3,742	4,440	8,935	9,948
Lower Silesia . . . . .	4,448	5,008	8,236	8,666
Upper Silesia . . . . .	10,129	12,889	25,824	26,263
Saxony-Thuringia . . . . .	...	...	...	...
Altogether . . . . .	59,568	87,214	280,945	313,195

The recovery of by-products in the manufacture of coke has taken its widest extension in the Dortmund district (Rhineland). According to the official reports (as found in the *Chemische Industrie*) there was produced in that district as by-products from coke-ovens.

	1910.	1911.	1912.	1913.
	Tons.	Tons.	Tons.	Tons.
Ammonium sulphate . . . . .	2 0,223	236,220	280,060	327,490
Ammonium nitrate . . . . .	1,231	1,495	1,488	1,347
Tar . . . . .	515,272	569,862	699,111	686,104
Tar-pitch . . . . .	68,880	90,860	110,876	134,661
Anthracene oil . . . . .	20,570	27,296	31,484	29,887
Creosote oil . . . . .	17,264	21,509	24,579	22,845
Oil for lighting purposes . . . . .	12,833	18,035	25,855	23,333
Washing-oil . . . . .	1,810	2,320	4,366	15,203
Crude naphthalene . . . . .	7,954	9,855	13,864	12,823
Anthracene . . . . .	2,382	2,403	3,354	3,404
Crude benzol . . . . .	28,050	36,581	35,024	31,273
90 per cent. Purified benzol . . . . .	27,087	30,913	45,573	81,776
Pure benzol . . . . .	...	...	...	1,593
Crude toluol . . . . .	2,584	2,302	2,585	2,115
Purified toluol . . . . .	794	1,656	3,910	5,452
Pure toluol . . . . .	...	...	...	1,130
Crude xylol . . . . .	1,483	1,536	1,927	1,981
Solvent naphtha, crude . . . . .	867	1,571	1,933	2,437
" " purified . . . . .	...	...	6,437	9,520
Illuminating gas . . . . .	Cubic metres. 43,105,249	Cubic metres. 84,594,853	Cubic metres. 162,613,953	Cubic metres. 137,954,840

The following figures on the coke industry in the United Kingdom are taken from *J. Soc. Chem. Ind.*, 1907, p. 1230.

Production of blast-furnace and gas-works		1905.	1906.
coke . . . . .	tons	18,037,985	19,296,256
Coking coal consumed . . . . .	"	33,452,943	35,402,677
Number of coke-ovens } in operation . . . . .	Beehive . . . . .	25,314	23,454
" " . . . . .	Coppée . . . . .	2,233	2,308
" " . . . . .	Simon-Carvès . . . . .	726	808
" " . . . . .	Otto-Hilgenstock . . . . .	503	768
" " . . . . .	Semet-Solvay . . . . .	470	670
" " . . . . .	Koppers . . . . .	72	108
" " . . . . .	Simplex . . . . .	78	78
" " . . . . .	Bauer . . . . .	52	52
" " . . . . .	Other types . . . . .	1,412	1,482

Returns made by 257 coking plants show that 51 of these recovered their by-products.

The number of new by-product ovens in course of construction in 1906 was: 320 Semet-Solvay, 15 Otto-Hilgenstock.

In Belgium in 1905, according to Haarman, as much as 80 per cent. of the coke was made in by-product ovens; in France, much less; in Great Britain (in 1903), 10 per cent.; in the United States, 7.5 per cent.

In the United States in 1901 the total quantity of coke produced was 21,495,883 tons, of which only 1,179,900 tons were made in 1165 by-product ovens (*Iron Age*, 24th July 1902).

In 1905 there were in the United States 2380 by-product ovens on the Otto-Hoffman system, and 1255 on the Semet-Solvay system (*Min. Ind.*, xiv., 350). The production in the United States of coal-tar was, from gas-works, 41,726,970 gall.; from coke-ovens, 25,771,115 gall. (Atwati in *J. Amer. Chem. Soc.*, 28, 1240).

The by-product coke-ovens in the United States produced in 1905, 26,223,323 gall. of coal-tar, 14,083 tons sulphate of ammonia, 4,294,468 gall. ammoniacal liquor, and 4463 millions cub. ft. of surplus gas.

The following figures are given in the *United States Geological Survey* for 1907, pp. 773 *et seq.* :—

	1905.			1906.		
Total production of coke in the U.S., short tons	32,231,129			36,401,217		
Of these, were produced in by-product ovens . . . . .	3,462,348			4,588,127		
Number of by-product ovens working . . . . .	1901.	1902.	1903.	1904.	1905.	1906.
Do. in construction	1165	1663	2061	3015	3159	3603
	1533	1346	1335	822	417	112
Beehive ovens in operation in 1903 :	75,232, building			.	.	4940
New beehive ovens completed in 1906 . . . . .				.	.	5893
" " in course of construction, 1906 . . . . .				.	.	4407

Of the 3603 recovery coke-ovens existing in 1906, 1295 were of the Semet-Solvay type, 1890 Otto-Hoffman, 362 Rothbery, 56 Newton-Chambers (these were not working). In course of construction: 112 Otto-Hoffman ovens, none of the other types. In 1907, 1000 retort ovens were to be built at Gary, Ind., in connection with new steel-works.

*General Remarks.*

For a long time the iron-makers considered the by-product coke as less valuable for their purposes than that from open ovens, but this prejudice seems to have ceased now, at least in Germany.

The general spreading of the by-product coke-ovens is, of course, kept back by the considerably higher expenses of the plant, and the much greater requirements to be made of the supervision and the skill of the men, in comparison with the open ovens, in some cases also by the difficulty of disposing of the by-products at remunerative prices. This makes it intelligible, that even in Germany until recently new coke-works have been erected on the old, open plan, since there seemed to be no chance of deriving a sufficient revenue for the much higher capital required for a recovery plant.

*C. Tar (and Ammonia) from Gas-producers.*

Since it had been proved that the process of coking coal can be performed to advantage in connection with the recovery of tar and ammonia, it was a very natural idea to extend this recovery to the gas from "gas-producers" or "generators." Attempts to solve this problem have been made in various quarters, but we shall here mention only the process of Sutherland and Mond.

Sutherland (B. P. 3891, 1883) adds to the coal a substance capable of evolving hydrogen, and at the same time giving out an acid. He prefers for this purpose a solution of calcium chloride. Superheated steam is also employed, by combining two gas-producers with a continuous superheater and a steam-supply, the heated gas from one of the producers doing the superheating work; the hot steam, passing through the second producer, causes therein an action between the carbon of the fuel and the steam, whereby "water-gas" is produced. The gases are passed through suitable apparatus for separating the tar and ammoniacal products. The details of the producer and superheating apparatus cannot be given here.

An examination of the tar from Sutherland's gas-producers has been made by Watson Smith (*J. Soc. Chem. Ind.*, 1884, pp. 9 and 64). Its specific gravity is 1.08; it is more like ordinary gas-retort tar than Jameson coke-oven or blast-furnace

tar, but it has a different smell. By distillation there was obtained from it :—

Below 230° . . . . .	5.44 per cent. by vol. oil of sp. gr.	0.956
From 230° to 300° . . . .	10.10       "       "       "	0.996
From 300° till oils solidified	14.48       "       "       "	0.990
Oils solidifying on cooling .	10.40       "       "       "	0.996
Coke . . . . .	30.50 per cent. by weight.	
Loss and water . . . . .	32.60       "       "	

On redistilling the first three fractions there was obtained :—

Below 160° . . . . .	0.16 per cent. by vol. on tar of oil.	
A. 160° to 210° . . . . .	0.90       "       "       "	
B. 210° to 220° . . . . .	2.04       "       "       "	
C. 220° to 230° . . . . .	15.50       "       "       "	
300° till oils begin to solidify	6.96       "       "       "	
Soft paraffin scale . . . .	2.76       "       "       "	

The oils A B C were light yellow, but darkened on standing. There was some phenol present, but no carbolic acid could be separated out. Naphthalene and anthracene were absent; of benzene, but little, if any, was present. Of paraffin, 6.7 per cent. on the tar could be separated.

The Sutherland-producer tar is thus seen to be entirely different from gas-tar, and is very similar to the Jameson-oven tar, but more impure than this. It is so thick that it can hardly be employed directly for creosoting without redistilling.

Several patents have been obtained by L. Mond for separating tar and ammonia from producer-gas, but as the principal stress is here evidently laid on the recovery of the ammonia, and the quality of the tar is not likely to be essentially different from that of the Sutherland-producer tar (a low temperature being expressly insisted upon), we shall treat of that process only in Part II.

It should be noted that, apart from the patents actually taken out, attempts have been made in various quarters to recover by-products from producer-gases, but none of them with any financial success. The examination of a producer-tar (not derived from Sutherland's producers, but from another source), according to a private communication made to me, has shown that it contained a comparatively large quantity of anthracene, but unfortunately at the same time so much

paraffin that it would be impossible on a manufacturing scale to oxidize the anthracene to anthraquinone; while, on the other hand, the paraffin obstinately retained some anthracene in spite of all purifying processes—the two substances thus mutually destroying their value.

As far as *tar* is concerned (not to speak of *ammonia* in this connection), it is clear that it would be entirely hopeless to seek for it in the producer-gases obtained from coke, anthracite, or very little bituminous coal. But precisely these are otherwise the best material for making producer-gas; bituminous coal causes difficulties in gas-producers just on account of the tar stopping up the outlets, pipes, etc. In any case, it is doubtful whether it will ever pay to construct the producers in a suitable manner, and to provide them with cooling and washing plant, and to undergo the loss of heat in these operations, merely to get some tar from bituminous coal. With ammonia the problem is different, as proved by the success of the Mond gas-producer, of which we shall treat in the part of this book devoted to ammonia.

A. Moore and the Dowson and Mason Gas Plant Co. (B. P. 2650, 1914) recover tar and ammoniacal liquor from producer-gas by cooling it down to  $38^{\circ}$  to  $71^{\circ}$  in an air-cooled condenser, passing it through a tar-extractor and a second air-cooled condenser at a higher level. The tar and liquor from the extractor and second condenser flow back through the first condenser in the reverse direction to the hot gas, whereby the tar is dehydrated. The tar and ammoniacal liquor are separated by decantation, and the latter is passed first through a heat exchanger, where it heats the water for the producer-jacket, and then through a scrubber in the reverse direction to the gas from the second condenser. A strong ammoniacal liquor is thus obtained.

#### D. *Tar (and Ammonia) from Blast-furnace Gases.*

The great majority of blast-furnaces are fed with coke, and it is evident that we cannot expect to recover either tar or ammonia from the waste gases of such furnaces. But it is otherwise with furnaces fed with raw coal, in which the upper part of the furnace may be said to constitute a



coking-chamber. Such an instance occurs in the West of Scotland, where there are vast beds of coal, known as "splint-coal."<sup>1</sup> This coal is admirably adapted for direct use in blast-furnaces, since certain varieties of it agglomerate very little during coking and do not decrepitate. Scotch splint-coals contain on the average 40 per cent. of volatile matter, of which 28 to 35 go to form tar, gas, etc., and they yield on the average 50 to 55 per cent. of fixed carbon. If the average amount of nitrogen they contain (1.35 per cent.) were all evolved as ammonia, this would correspond to 142½ lb. of pure sulphate per ton (6.36 per cent.); but in blast-furnace practice only from 17 to 20 per cent. of the nitrogen of the coal is converted into ammonia. As early as 1845 Bunsen and Playfair recommended the recovery of such ammonia from blast-furnace gases, and calculated that the Alferton furnace would yield 9½ kg. per ton. W. Jones makes the following calculation for the Scotch blast-furnaces:—Each ton of coal may be said to yield, on an average, 16 per cent. of its nitrogen as ammonia, that is, equal to 22.8 lb. of ammonium sulphate, and from 120 to 220 lb. of tar, partly in the form of vapour at the temperature of the escaping gases, partly in the state of suspension. These substances, along with a very considerable amount of dust (which must be got rid of before tar and ammonia are condensed), are contained in a volume of gas corresponding to 125,000 cub. ft. at 15°.5; but as the actual temperature varies from 204° to 343°, the gas will at, say, 260° C. occupy over 230,000 cub. ft., increased by 300 to 400 lb. of water per ton of coal in the form of vapour. This is thirteen times the volume of gas per ton of coal compared with that obtained in the manufacture of illuminating gas in ordinary fireclay retorts.

From this enormous volume of gas issuing out of the blast-furnace throat, the tar and ammonia are to be condensed. For this purpose, it is best, according to experience, to maintain an outward pressure on the gas. A suction or inward pressure may not only lead to disastrous explosions, but it very much reduces the yield of ammonia, owing to the entrance of air and the consequent combustion of the ammonia. The tar in the gas is scrubbed out with great difficulty, on account of its

<sup>1</sup> W. Jones, *Proc. Iron and Steel Inst.*, 1885; *J. Soc. Chem. Ind.*, 1885, p. 737, where analyses of such coal are given.

peculiar physical condition and its state of suspension in such a large volume of gas. No amount of cooling and washing is so effective as some form of violent mechanical action, such as dashing with water or otherwise.

If the whole of the gases of the furnaces at present in blast in Scotland were to be treated for the recovery of ammonia, the turn-out of ammonium sulphate would already in 1885 have been some 18,000 tons per annum, equal to 22 per cent. of the production of Great Britain at that time.

The different methods for recovering volatile products from blast-furnaces may be grouped as follows:—

(I.) Methods depending on the condensation or cooling of the gas.

- (a) Alexander and M'Cosh process, as practised at the Gartsherrie Iron-works.
- (b) Dempster process (B. P. 11250, 1884).
- (c) Henderson process.

(II.) Methods depending upon the use of acids, without the cooling of the gas.

- (a) Neilson's process, or Summerlee method (B. P. 440, 1882).
- (b) Addie's process, or Langloan method (B. P. 4758, 1882).
- (c) Chapman's process (B. P. 6406, 1884).
- (d) Main and Galbraith's process (B. P. 10448, 1884).

Most of these processes principally, or even exclusively, tend to the recovery of the ammonia only, and will therefore be mentioned in Part II.; in this place we shall describe the principal process by which tar or oil can also be obtained from blast-furnaces.

The *Gartsherrie process* (Alexander and M'Cosh's patents, B. Ps. 4117, of 1879; 1433, of 1880; 3785, of 1881) is illustrated by Figs. 28 and 29. The gases pass from the furnace by the main pipe G, through pipes g, the number of which is in proportion to the temperature and amount of the gases, into the coolers K, consisting of series of upright tubes, connected with each other alternately above and below, so that the gases take the course indicated by the arrows. Cooling takes place by

the large surface exposed by the pipes to the air. The pipe which connects the lower ends of these tubes also serves to collect condensed liquids, tar, and ammonia water; these

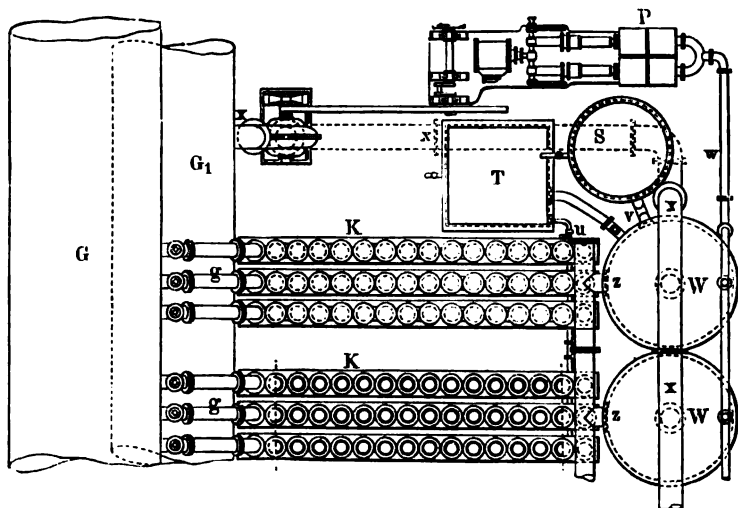


FIG. 28.

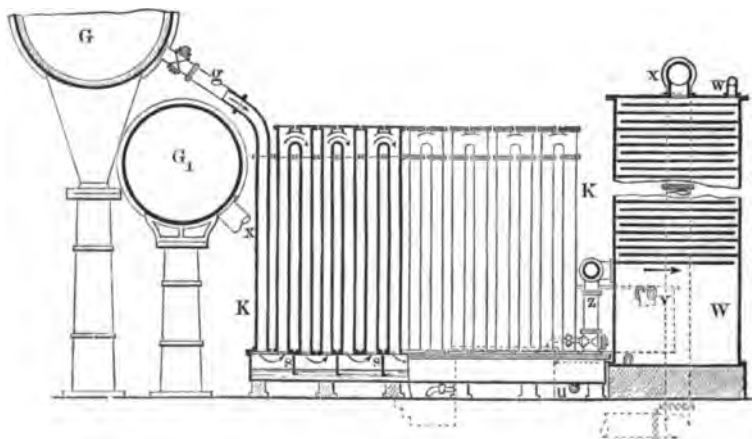


FIG. 29.

are not permitted to rise to such a height as to obstruct the passage of the gas, but are drawn off by the overflow-pipe *u* to the tank *T*. The whole, as we see, is practically a copy of

the ordinary air-condenser employed at gas-works. The gases pass through  $z$  into the washing-towers or scrubbers W, provided with perforated shelves of wood or metal, leaving alternately an open passage on one side or the other of the scrubber. A stream of water trickles from  $w$  down these shelves; the tar and ammonia, which have escaped condensation in K, are here condensed partly by the action of the water spread over a large surface, and partly by the continuous impact against the shelves, and pass down from W into T and S. The aqueous liquid which collects in S is pumped by P to the top of the towers, and used repeatedly, until sufficiently enriched with ammonia. The cooled and washed gases proceed by  $x$  to the second main  $G_1$ , to be utilized as required. If it be desired simply to eliminate flue-dust, the towers are unnecessary; but it is advisable in such a case to moisten the gases before they enter the coolers. A special apparatus for this purpose has been described by Belani.<sup>1</sup> I. Alexander has also constructed cooling and washing chambers of very great efficiency,<sup>2</sup> offering an extremely large area of water-cooled and air-cooled surface.

New patents for this purpose have been taken out by Mackay (No. 14060, 1889), the Coltness Iron Co. (No. 17673, 1889), and Imray (No. 10589, 1891).

The utilization of blast-furnace gases in Scotland is described in detail in the *Transactions of the Institution of Engineers and Shipbuilders in Scotland* for 1896, part 25, from which the following notes are taken:—A plant for treating the gases from four blast-furnaces has to deal with upwards of 35 millions of cubic feet per 24 hours. The collecting-pipe is 7 ft. 6 in. wide, and is connected with several exhausters. The pipes are lined with firebricks, and first lead to a tar-washer, a square box with a sloping bottom, divided by partitions into several chambers. The partitions are nicked out at the bottom, where they dip into the tar and compel the gases to find their way through this in a multitude of small streams. This promotes an intimate contact between the tar and the gas, the complete separation of the particles of tar suspended in the gas, and, in consequence of the high temperature, the dehydration of the tar.

The gases leave this apparatus at a temperature of about

<sup>1</sup> *Dingl. polyt. J.*, vol. cliv., p. 257; *J. Soc. Chem. Ind.*, 1885, p. 218.

<sup>2</sup> *Ibid.*

55° C., and enter the "condenser," consisting of eight sets of eighteen pipes each, 50 ft. high and 18 in. wide. The gases are made to circulate up and down, and leave the last pipes with a temperature of 22°. During hot weather the upper parts of the pipes are cooled by sprinkling water upon them. The tar and ammonia condensed here are separated by lying undisturbed in a "separator." The gases now pass another "washer," 60 ft. long, 12 ft. wide, and 7 ft. high, fed with ammoniacal liquor, which is here made sufficiently strong for working up into sulphate of ammonia, and the tar condensed is used in the "tar-water" previously mentioned. Behind this are fixed the three exhausters, each with a capacity of nearly a million cubic feet of gas per hour and provided with pressure-gauges. The gas, after passing the exhausters, is lastly forced through another washer, fed with water and intended to retain the remaining ammonia and tar; the liquors condensed here are used for feeding the preceding washers. The purified gas then passes on to the steam-boilers and the heating-stoves for the blast, where it is burned.

The tar is distilled in stills uniformly heated with purified gas; the ammonia-water is distilled in column-apparatus by means of steam, and the ammonia converted into sulphate.

From each ton of coal fed into the blast-furnaces is obtained 7 gall. of tar-oil, 86 lb. of tar-pitch, and 25 lb. of sulphate of ammonia. The purified gas suffices for raising all the steam required for the blowing-engines, for working part of the regenerative blast-heating stoves, for distilling all the tar, and for evaporating part of the washings from the ammonia-stills.

At a meeting of the Iron and Steel Institute, held 5th and 6th May 1898, Riley reported that on an average from 1 ton of coal 130,000 cub. ft. of gas is obtained; the by-products represent 20 per cent. of the price of the coal. The gas (as confirmed by Mond) is perfectly well adapted for gas-motors, which are in constant use up to 250 h.p., with a saving of 45 per cent. as compared with the coal burnt under steam-boilers. The cost of plant is considerable, but it is quickly repaid by the profits.

In 1891 there were 77 blast-furnaces in Scotland (*Alkali*

*Reports*, 1891, p. 13), working with coal suitable for the recovery of tar and ammonia, 57 of which were provided with recovery-plant. Whilst a blast-furnace of average size, including the blowing-engines, cost £7800, the condensing-plant alone costs more than that; the 57 plants in question have cost £444,600. In England three blast-furnaces are provided with recovery-plant, at a cost of £12,000 per oven.

The following process described in the *Zeitschr. f. Berg-, Hütten- und Salinenwesen*, 1895, p. 172, as being employed at an English iron-works, present some interest. Beside the blast-furnaces there is a kiln, 15 ft. high, charged with 50 per cent. pyrites, which is kept burning by a blast of air. The mixture of air and sulphur dioxide thus formed is introduced into the pipe carrying away the blast-furnace gas, and here sulphate of ammonia is formed. The hot gases are now passed through a tower filled with shelves over which water is constantly run. The liquor here formed is pumped up again until it is sufficiently strong, and ultimately the solution of sulphate of ammonia is separated from the tar by settling.

A paper by R. Hamilton in the *Journal of the West of Scotland Iron and Steel Institute*, No. 4, January 1902 (*Stahl u. Eisen*, 1902, p. 509), reports on the present state of the recovery of by-products from the Scotch blast-furnaces. We give a brief *résumé* of this very interesting paper (which necessarily treats of ammonia as well as of tar). During the twenty years since the introduction of this new industry, more progress has been made in erecting new plants and extending those formerly built than in further improvements of the process. The Gartsherrie process of Alexander and M'Cosh (p. 171), which is working since 1881, has proved the simplest means, viz., cooling the gases and washing with water, suffice for a complete recovery of the by-products. At first the tar, whose quality is entirely different from that of gas-tar, was almost unsaleable; later on, certainly, uses have been found for it as well. This led to the invention of Addie's "Langloan" process, which aimed at producing merely ammoniacal compounds, by bringing the gas into contact with  $\text{SO}_2$  (from burning pyritic shale). This process worked from 1884 till 1892, but the difficulties were too great, and it was definitely abandoned in favour of the Dempster process.

A similar process was tried but given up again, at the Summerlee Iron Works. The gases were not cooled, but at once brought into contact with sulphuric acid. Main and Galbraith's process, which works with hydrochloric acid, as well as a process invented by Hamilton himself, where ammonium carbonate is produced, have no interest with respect of the recovery of *tar*. Hamilton then quotes a number of experiments, bearing on the influence of the *water* contained in the ore. This, of course, would influence the yield of ammonia much more than that of the tar, but it is felt even with respect of the latter. English ores containing much water produced much less ammonia from the same coal than the Scotch ores, containing less water. But by roasting the English ore *no* improvement in the yield of tar and ammonia was effected; the cause of this behaviour of the English ore has not yet been cleared up. When the coal was distilled by itself, it yielded 214 lb. tar per ton. When mixed with English ore in the same proportion as in the blast-furnace, the yield of tar fell to 66 lb., and of the  $\text{NH}_3$  44 per cent. was lost. Scotch ore acted in a similar way. If in lieu of ore, sand was mixed with the coal, 170 lb. of tar was obtained, which proves that the loss of tar and  $\text{NH}_3$  is not attributable to the mere presence of foreign solid matter.

The total quantity of tar recovered from the gases of the Scotch blast-furnaces in 1900 is estimated by Hamilton at 120,000 tons (along with 16,559 tons sulphate of ammonia).

Neilson (B. P. 28508, of 1904) recovers the tar from blast-furnace gases by means of a washer, provided with a wire-gauze partition, dipping into creosote oil. According to his B. P. 28462, of 1908, he facilitates the removal of tar-pitch or other substances suspended in the gas by previously gasifying the creosote oil used as a washing agent. The blast-furnace gases, thereby purified from tar, are then employed for working gas-motors.

Hartenstein and Weber in 1809 took out the French patent No. 273776 for the removal of the waste substances contained in blast-furnace gases.

*Composition of Blast-furnace Tar.*—The tar recovered from blast-furnaces has been repeatedly examined by Watson Smith (*J. Soc. Chem. Ind.*, 1883, p. 495; *J. Chem. Soc.*, 1886, vol. xlix.,

p. 17). Its specific gravity was found = 0.954. Distillation yielded:—

	Per cent. by volume.	Per cent. by weight.	Sp. gr.
Below 230° { Water . . . . .	30.60	32.3	1.007
{ Oil . . . . .	2.91	2.8	0.899
230° to 300° . . . . .	6.97	7.1	0.971
300° until oils solidify . . . . .	13.02	13.5	0.994
Oils solidifying on cooling (soft paraffin scale) . . . . .	16.75	17.3	0.987
Coke . . . . .	...	21.5	...
Loss . . . . .	...	5.5	...

The oils were quite transparent, the lower-boiling and lighter fractions possessing an amber-yellow colour, the higher-boiling ones having a colour approaching that of port wine. On standing a day or two they all considerably deepened in colour, especially the heavier fractions, which possessed a strong green fluorescence.

A further examination of the distillates proved that naphthalene is present in very small quantity; anthracene could not be detected, but small quantities of toluene, xylene, and pseudocumene were isolated. The xylene proved to consist principally of the meta-isomer (priv. comm. from Watson Smith). About 0.54 per cent. of hard paraffin was obtained from the tar, and a considerable amount of phenols, among them true carbolic acid. By successive treatment with caustic soda and sulphuric acid, the distillates answering to the carbolic oil and creosote oil of ordinary coal-tar yielded 23.1 per cent. by volume of phenols, and 11.09 per cent. by volume of basic substances.

This large proportion of phenols, far exceeding what can be obtained in a similar manner from ordinary gas-retort coal-tars, seems to some extent to confirm the theory of K. E. Schulze (Liebig's *Annalen*, vol. ccxxvii., p. 143), according to which at least a considerable proportion of the aromatic coal-tar hydrocarbons is formed by the breaking-up, at higher temperatures, of first-formed phenols into the elements of water and hydrocarbons. Since blast-furnace tar, both on account of its being formed in the top part of the furnaces and also because of its chemical and physical properties, is evidently a low-temperature product as compared with the tar obtained from



gas-retorts and close coke-ovens (Carvès', Otto's, etc.), it might *a priori* be supposed that it was an intermediate mixture, and to contain, so to speak, the half-way phenol constituents in predominating quantity. On the contrary, it contains but a small quantity of the lowest phenol (carbolic acid),  $C_6H_5.OH$ , and cresols,  $C_6H_4(CH_3).OH$ , much less than gas-retort tar, which would seem to show that Schulze's theory can hardly extend to the formation of benzene itself. The decomposition of the higher-boiling phenols of blast-furnace tars by means of hot zinc-dust or hot iron-borings yielded a large quantity of xylenes, and proved the original presence of metaxyleneol,  $C_6H_3(CH_3)_2.OH$ , in accordance with Schulze's theory; the still higher-boiling fractions, treated in the same way, indicated the presence of pseudocumenol,  $C_6H_2(CH_3)_3.OH$ , and of naphthols,  $C_{10}H_7.OH$ . Of course other phenols and phenol-ethers might also be present. Similar results were obtained by Allen with blast-furnace tar.

In any case, blast-furnace tar is altogether different from ordinary gas-retort tar, and cannot be employed for the same purposes. It would require to be redistilled, and would then yield creosoting oils of good quality and lubricating oils of indifferent quality.

*Uses of Blast-furnace Tar.*—Allen and Angus (B. P. 11680, of 1887) distil blast-furnace tar, extract those constituents of the distillate which are soluble in alkali, and precipitate the solution by means of carbon dioxide, in the shape of furnace-gases. By repeated solution and fractional precipitation, as well as by fractional distillation, the products are separated. The volatile products are used as disinfectants, the heavy products for pickling timber. The hydrocarbons are worked up for paraffin oil, lubricating oil, and gas-oil. (This patent contains nothing which had not been previously known.)

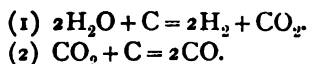
Blast-furnace creosote oil is now largely used, especially in Scotland, for pickling timber, for the "lucigen light" (which will be described in a subsequent chapter), and as fuel. The phenols contained therein (25 to 35 per cent. against 5 to 10 per cent. in heavy gas-tar creosote oil) resemble those from wood-tar, lignite, or shale oil; they are sold as an antiseptic, under the name of "neosot," and are said to be equal in antiseptic powers to

"liquid carbolic acid," but with much less corrosive properties (*Chem. Trade J.*, 1887, p. 122). This was confirmed by a new investigation by Watson Smith (*J. Soc. Chem. Ind.*, 1887, p. 583). The tar from the Gartsherrie blast-furnaces is rather lighter than water; it contains much paraffins, but anthracene could not be discovered, perhaps owing to the presence of the paraffins. The quantity of phenols is very large; besides phenol proper we find metacresol, metaxyleneol, pseudocumenol, and naphthols. The hydrocarbons found were: toluene, xylene (over 70 per cent. metaxylene), pseudocumene, mesitylene, and, a little naphthalene; benzene was never found in such tar, but is perhaps present in the gases. The basic constituents resemble those of coal-tar; aniline was found among them.

*E. Tar obtained in the Manufacture of Water-gas.*

This manufacture, which is especially flourishing in the United States, is now also carried on to a considerable extent in Europe; consequently "water-gas tar" is also coming into the market, especially in America.

Water-gas is obtained by the action of superheated steam on white-hot coke or anthracite, by the reactions:



The mixture of carbon monoxide and hydrogen thus obtained does not burn with a luminous flame, but with a light blue flame, which caused that gas to be called "blue water-gas." It can be employed in that state for heating purposes, but for lighting purposes it must be "carburetted" by means of volatile hydrocarbons. This is usually done by passing the gas, together with the vaporized hydrocarbons, through red-hot retorts. In this process, if the superheater be not too hot, about 25 per cent. of the oil is recovered as tar, which is frequently run to waste (Douglas, *J. Gas Lighting*, 1891, p. 1130).

The industry of carburetted water-gas was first started in the United States, which in their immense petroleum fields possess an inexhaustible supply of hydrocarbons adapted to that purpose, and that industry attained a flourishing state in the United States already at a time when not a single plant

for it had been erected in Europe.<sup>1</sup> Among the various processes for manufacturing carburetted water-gas the most widely used are those of Lowe, of Dellwik and Fleischer, and of Bayenthal (Kölnische Maschinenbau - Aktiengesellschaft). According to Graefe a few years ago the production of oil-carburetted water-gas in the United States amounted to more than 1800 million cubic metres per annum. In Great Britain (*J. Gasbeleucht.*, 1910, p. 295) about 590 million cubic metres of carburetted water-gas are produced, mostly by the Lowe process, carried out by Humphreys and Glasgow in Great Britain, by the United Gas Improvement Co. in the United States, and by Julius Pintsch, A. G., in Germany. In 1910 the number of factories working on that plan was altogether 976, with a daily production of nearly 21 million cubic metres.

We cannot in this book describe the water-gas process itself, which belongs to the domain of gas industry, but we have to speak of the *tar* obtained therein.

According to Graefe (*loc. cit.*), the quantity of gas-oil used for carburetting one cubic metre of water-gas is 400 to 450 g., 20 per cent. of which is recovered as tar. Douglas (*J. Gas Lighting*, 1891, p. 1130) puts the yield of tar = 25 per cent.

This tar contains about 50 per cent. water, with which it forms an emulsion not separable by the usual means. Douglas has succeeded in separating the oil from the water by heating the tar in closed boilers at a pressure of 10 atmospheres. He thus obtained from 100 parts of crude tar, 50 parts dehydrated tar with only 1 per cent. moisture, and 25 parts water, the remainder of the water evaporating during the process. According to Douglas, this dehydrated tar is readily saleable, but he does not say what is done with it.

According to *J. Gas Lighting*, 1915, p. 196, the water-gas tar is dehydrated at the Amsterdam Western Gas-works by centrifugalling. The first experiments were unsuccessful, but by working at higher temperatures, very satisfactory results were obtained. The difference in specific gravity between water-gas tar and water increases considerably with the rise of temperature. The centrifugal machine used has a drum revolving at a high rate of speed on a vertical shaft; at

<sup>1</sup> Hempel, *J. Gasbeleucht.*, 1887, No. 17; Graefe, *Petro'eum*, 1907, p. 193.

the upper part of the interior of the drum is fixed a flat ring, 4 in. wide, fitted so that a small space is left between the inner surface of the drum and the outer circumference of the ring. The tar travels upwards along the inner surface of the drum to the upper surface of the ring, and thence to the tar off-take. The water, being lighter, forms a layer at the side of the tar, and travelling upwards its passage is barred by the ring, so that it is forced along the under side of the ring where the water outlet is fixed. The temperature necessary for the perfect dehydration of the tar is between  $60^{\circ}$  and  $70^{\circ}$ , which is obtained by pre-heating the tar in a rectangular tank fitted with an outlet pipe for the escape of any gaseous products. The heated tar has often a water content of about 60 per cent., which is reduced to less than 1 per cent. in one operation. Water-gas tar emulsions containing 80 to 90 per cent. of water have been treated in the same apparatus, the working temperature being  $95^{\circ}$  to  $100^{\circ}$ , no trouble due to evaporation being experienced at this temperature. The tar obtained has a very low content of "free carbon," viz., 0 to 4 per cent., and the average calorific value is 17,200 B. Th. U. per lb. The working costs of the treatment are particularly low, and owing to its uniform character the tar is used largely as a substitute for mineral-oil fuel, and commands better prices than those obtained for tar not centrifugally treated.

A. H. Elliott (*Amer. Chem. J.*, 1884, p. 248) obtained the following results with water-gas tar :—

Specific gravity, 1-100.

400 c.c. on fractional distillation yielded per cent. by volume :—

Fraction	I., $80^{\circ}$ to $200^{\circ}$ .	. . .	9.2	{ $\frac{1}{3}$ oil. $\frac{2}{3}$ water.
"	II., $200^{\circ}$ „ $270^{\circ}$ .	. . .	{	11.2 solids. 17.7 oil.
"	III., $270^{\circ}$ to the formation of pitch	. . .	{	6.0 solids. 26.5 oil.
"	IV.	. . .	{	1.7 semi-solid mass. 6.0 oil.
			<u>78.3</u>	

The solid portion of fraction II. consisted principally of naphthalene, and contained only 0.82 per cent. anthracene = 0.09

per cent. of the weight of tar. From fraction III. 2.33 per cent. anthracene of the weight of tar could be obtained. The solid portion of this fraction was a greenish-yellow mass, containing 25.6 per cent. anthracene; the oils contained only 3 per cent. anthracene. Fraction IV. still yielded about 2 per cent. anthracene, almost equally divided between the semi-solid portion and the oil. Thus the total percentage of anthracene would amount to 2.63 per cent. of the tar—that is, from six to ten times as much as in coal-tar.

Nevertheless this tar seems to possess but little value. According to a communication from Mr S. B. Boulton, water-gas tar, which is frequently mixed with London gas-tar, contains so much paraffins that the preparation of anthracene from such a mixture is unremunerative, and buyers therefore object to getting water-gas tar with coal-gas tar. It is also mixed with so much water (50 to 75 per cent.), that it forms an emulsion which is difficult to separate even on prolonged standing. But Vivian B. Lewes states (*J. Gasbeleucht.*, 1902, p. 329) that the introduction of water-gas into coal-gas retorts has an influence merely on the quantity, not on the quality of the tar.

Mathews and Goulden (*Gas World*, xvi., p. 625) found in water-gas carburetted with Russian crude oil:—

	Per cent.
Benzene . . . . .	1.19
Toluene . . . . .	3.83
Light paraffins . . . . .	8.51
Solvent naphtha . . . . .	17.96
Phenols . . . . .	trace
Middle oils . . . . .	29.14
Creosote oil . . . . .	24.26
Naphthalene . . . . .	1.28
Anthracene (crude) . . . . .	0.93
Coke . . . . .	9.80
	<hr/>
	96.90
	<hr/>

The percentage of anthracene in this case is also very high. Downs and Dean<sup>1</sup> examined samples of tar, taken from various parts of a plant for producing carburetted water-gas by Lowe's

<sup>1</sup> *J. Ind. Eng. Chem.*, 1911, pp. 108 *et seq.*

process, by means of a spray of gas-oil. Of that oil about 25 per cent. remained undecomposed, which during the purifying process were partly retained in the tar. The tar from the receiver and the wood-grate washer is called "deposited tar"; that from the water-cooler, "condensed tar." Their examination was carried out on four samples: (1) deposited tar (about 60 per cent. of the total tar), sp. gr. 1.090; (2) condensed tar, sp. gr. 1.081; (3) tar from the Pelouze-Audouin tar-separator, sp. gr. 1.068; and (4) washing-tar from the revolving washer, which is provided with a preliminary air-cooler, sp. gr. 1.056 at 15°·5 C. All the samples contained only traces of free carbon, and 0.08 per cent. nitrogen. As is proved by the specific gravities, the percentage of higher and lower boiling constituents differs in this way: that the latter increase in quantity from the deposited tar to the washing-tar. The samples commence boiling below 100°, and yield up to 200° from 3 to 15 per cent.; between 200° to 240°, from 15 to 45 per cent.; and up to 360°, from 60 to 70 per cent. distillates. The lower-boiling fractions are of a faint yellow colour, clear and liquid; the naphthalene of the intermediate fractions, separating out at the ordinary temperature, possesses a pure white colour, and the high-boiling fractions are also much less coloured than the corresponding fractions of ordinary coal-tar. The water-gas tar contains on the whole much less solid constituents than the coal-tar; these occur only in the fractions boiling above 300°. The distillates of the samples taken in various places differ more in quantity than in quality.

Downs and Deane later on (*J. Ind. Eng. Chem.*, vi., p. 366, 1914) showed, by systematic fractional distillations of water-gas tar, that its hydrocarbons are similar to those of coal-tar, but the bases, phenols, and free carbon are absent. It contains no paraffins. The difference from coal-tar in the quantity of haloids absorbed points at a different percentage of non-saturated compounds outside the benzene series. Benzene, toluene, xylene, mesitylene, naphthalene, and anthracene were proved to be present in varying quantities. The preparation of pure hydrocarbons and of commercial products was attained by methods similar to those employed for coal-tar, without any special difficulties. Water-gas tar might come into question

for supplying benzol and solvent naphtha. Naphthalene could be easily obtained from it, but there is no corresponding demand, nor are the commercial conditions favourable to the preparation of anthracene.

*Working up the Water-gas Tars.*—Scholvien, in a German patent of 1904 (No. 163623), states that the water-gas tar obtained in the treatment of petroleum hydrocarbons, for the purpose of preparing carburetting agents, cannot be distilled on account of its large percentage of water, and had hitherto merely been utilized for making pitch or as fuel. Even when mechanically dehydrated, it can be distilled only on a small scale. He treats it, therefore, by a special process (Ger. P. 161236), of which we shall speak in Chapter V.

The German water-gas tars have a specific gravity differing but little from water; they are thin, oily, and of brownish-black colour. On working up on a large scale, a tar, after removing from 10 to 20 per cent. of water, yielded:—

(a) Light oils up to 230°	.	.	.	22.0 per cent.
(b) Heavy " " 300°	.	.	.	30.0 "
(c) " " from 300° to 330°	.	.	.	13.0 "
(d) Pitch (very shiny and easily fusible)	.	.	.	30.0 "
Loss	.	.	.	5.0 "
				<hr/> 100.0 per cent.

The heavy oils (b) deposited on prolonged cooling 0.5 per cent. (of the weight of tar) crude naphthalene, and the oils boiling from 300° to 330° (c), 0.13 crude anthracene, containing 40 per cent. pure anthracene.

In Germany only very little water-gas tar is worked up by distillation; most of it is used at the gas-works themselves for purifying the illuminating gas from naphthalene, or as fuel for Diesel motors, etc. In America, Sadtler has recommended the heavy distillates for pickling timber (*Chem. Eng.*, x., p. 74). Forrest points out (*J. Soc. Chem. Ind.*, 1911, p. 193) that there is no possibility of procuring a sufficient quantity of water-gas tar for that purpose. He quotes the results of examining the samples of water-gas tar and separating the fractions by distillation, comparing them with coke-oven tar. The oils are practically free from naphthalene, and quite liquid at 95°.

F. *Tars and Tar-products obtained by Superheating Certain Oils and Vapours (Oil-Gas Process).*

The decomposition of compounds belonging essentially to the "fatty" ("aliphatic") series, by passing their vapours through red-hot tubes, and the fact that aromatic compounds are formed in this way, has been studied by Berthelot (since 1867) and several other chemists. The preparation of illuminating gas, which always contains considerable quantities of aromatic compounds, from oil and other fatty substances has been practised according to this method for a long time. This process, the "*oil-gas process*," seems to have been invented by John Taylor, in 1814,<sup>1</sup> and was introduced into Germany in 1828, but soon mostly abandoned, since the oil was found to be too expensive. It was taken up again after 1850, when cheap mineral oils, from shale and lignite, came into the market; and in America the refining of petroleum yielded a large quantity of oil suitable for the above purpose. The oil-gas industry was principally developed in Germany by H. Hirzel, Hübner and others, but chiefly by Julius Pintsch, whose compressed oil-gas has been widely employed for lighting railway carriages, both in England and Germany.

We cannot in this place enter into the details of the manufacture of oil-gas, and only mention that the raw material, the so-called gas-oil, has generally a specific gravity of 0.850 to 0.900, and has to pass over up to 320° C. According to Hirzel, 100 kl. gas-oil should yield 60 cbm. gas of an illuminating power of 7.5 German standard candles, with an hourly consumption of 35 litres.

For this purpose that oil, introduced into a red-hot retort, is first volatilized and the vapours are decomposed into more volatile bodies in contact with the hot walls of the retort. Part of the oil escapes decomposition and is condensed in a receiver; another portion is converted into aromatic hydrocarbons, with secretion of carbon, the former being also condensed in the receiver. Thus *oil-gas tar* is formed. According to Young (*J. Gas Lighting*, 1893, ii., p. 260), many paraffins are formed by the radiant heat within the retort, and mostly aromatic hydrocarbons by contact of the vapours with the hot

<sup>1</sup> Scheithauer, *Die Fabrikation der Mineralöle*, etc., 1895, p. 282.



sides of the retort; this should be taken into account when constructing apparatus, either with the view of producing an illuminating gas or obtaining benzol, etc.

The following table gives some idea of the percentage composition of oil-gas as compared with coal-gas:—

	Oil-gas.	Coal-gas.
Carbon dioxide . . .	1.0	1.5
Oxygen . . . . .	0.5	1.4
Heavy hydrocarbons . .	33.0	3.0
Carbon monoxide . . .	2.5	8.0
Hydrogen . . . . .	15.0	48.7
Methane . . . . .	40.0	33.7
Nitrogen . . . . .	2.0	4.0

On compressing oil-gas to 10 or 12 atmospheres, each 100 cbm. of compressed gas separate about 6 to 10 kl. liquid hydrocarbons. This liquid has been examined by Armstrong and by Bunte (*J. Gasbeleucht.*, 1893, p. 442), who found in it:—70 per cent. benzene; 15 per cent. toluene; 5 per cent. higher aromatic hydrocarbons; 10 per cent. olefins.

R. E. Wyant (*J. Gas Lighting*, 1914, cxxviii, p. 131) describes the recovery of oil-gas tar from the emulsion coming out of the tar-scrubber.

The oil-gas tar proper, of which 30 to 45 per cent. of the oil employed is obtained, is even now considered a troublesome by-product. In colour and smell it resembles coal-tar; but its specific gravity is 0.950 to 1.000, and it is much thinner. Its exact composition has not yet been ascertained, but it must vary very much, according to the raw material used, the temperature of its generation, and the shape of apparatus. Scheithauer quotes the following boiling-points:—

Between 70° and 150° C. . .	5 to 10 per cent.
„ 150° „ 200° „ . . .	5 „ 10 „
„ 200° „ 250° „ . . .	20 „
„ 250° „ 300° „ . . .	20 „
Above 300° . . . . .	30 „
Residue and loss . . . . .	10 „

The investigations of Scheithauer (*loc. cit.*), Pryce (*J. Gasbeleucht.*, 1893, p. 497), Macadam (*J. Gas Lighting*, 1893,

p. 400), Lewes (*ibid.*, p. 699), and Armstrong proved the presence of very small quantities of benzene, and rather more toluene and its homologues, but principally olefins and acetylenes, sometimes also low-boiling paraffins; also 3 to 4 per cent. naphthalene. Some oil-tars are entirely free from anthracene, others contain 0.06 up to 1 per cent. This anthracene contains considerable quantities of methyl-anthracene. Free carbon occurs in large quantities, but phenols and basic bodies are excluded by the nature of the raw material. Würth (*Untersuchungen eines Olgasteers*, München, 1904) found in oil-gas tar:—

	Per cent.		Per cent.
Benzene . . . .	1.00	Naphthalene . . . .	4.90
Toluene . . . .	2.00	Crude anthracene . . . .	0.58
Xylenes . . . .	1.30	Phenols . . . .	0.30
Resin-yielding oils boiling		Bases . . . .	traces
below 150° . . . .	1.00	Asphalte . . . .	22.0
Oils boiling from 150° to 200°	1.50	Free carbon . . . .	20.50
"      "      200° " 300°	26.60	Water (neutral) . . . .	4.00
"      "      300° " 360°	12.60		

Also all other constituents of coal-tar, excepting carbon disulphide and acridine, were proved to be present.

*Uses.*—Oil-gas tar is sometimes worked up by distillation. This process yields a light naphtha employed for carburetting gas, a middle fraction sold as "solvent naphtha," and a heavy fraction which is either employed for making new gas or as "boring-oil" in the iron industry. The residue forms a thick tar, much used instead of natural asphalt. Much of the oil-gas tar is burned at the gas-works, either mixed with other fuel or else by itself, by means of the "forsunka." Zimmer and Gottstein (Ger. P. 98061) work it up with Portland cement for the purpose of obtaining an extremely resisting material.

The principal use of that description of tar seems to be in the following direction. Although the discovery of benzene itself, by Faraday, was made in the year 1825 in the liquid condensing from compressed oil-gas, it is only quite recently that the *preparation of substances similar to coal-tar*—that is, containing considerable quantities of benzene, naphthalene, and anthracene—from the *heaviest distillates and residues of the petroleum and paraffin-oil refineries*, by *superheating* them in red-hot tubes, has been attempted on a practical scale. Special experiments to ascertain

how far this reaction might be applicable on a practical scale were made in response to a prize offered in 1877 by the Berlin Society for the Promotion of Industry. It was required to be shown that it is possible to convert the high-boiling oils of the browncoal-tar, by a technically applicable process, into the hydrocarbons forming the basis of the aniline-colour and alizarin industry.

Liebermann and Burg<sup>1</sup> found that the above oils, when passed through red-hot tubes filled with porous material, are converted into a mixture of hydrocarbons very similar to coal-tar, containing about 4 per cent. benzene and toluene and 0.9 per cent. crude anthracene. Petroleum and "vulcan oil" yielded much gas and benzene, but hardly any anthracene. Coal-tar oils, boiling between 140° and 150° and between 150° and 210°, when treated in a similar way, suffered much less loss of weight. The quantitative results obtained by those chemists are, from their own showing, no guide as to those obtainable on the large scale, for which special experiments would be required. Similar to the above were the results of Salzmann and Wichelhaus<sup>2</sup>; and Atterberg<sup>3</sup> proved the same for wood-tar.

The most extended paper on this subject has been published by Letny.<sup>4</sup> He examined a tarry condensate, produced in the manufacture of gas by passing heavy petroleum "tailings" through red-hot tubes filled with wood; after several passages through the retort he found it entirely similar to coal-tar, and especially proved it to contain benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene, along with unchanged petroleum. After this he tried passing the petroleum-tailings on a small scale through a red-hot tube filled with charcoal. He obtained 33.3 per cent. of gas and 66.6 per cent. of tar, containing much amylene, benzene, toluene, xylene, and higher-boiling oils, but no solid hydrocarbons. The absence of the latter was ascribed by Letny to the comparatively small thickness of the layer of red-hot charcoal which the petroleum-vapours had to pass on the small scale. At a higher pressure more oils of low boiling-point were formed, but on the whole less tar and bad gas.

The raw material for Letny's experiments was the residue from refining the petroleum of Baku in South Russia. Since

<sup>1</sup> *Ber.*, 1878, p. 723.

<sup>3</sup> *Ibid.*, p. 1222.

<sup>2</sup> *Ber.*, pp. 802, 1431.

<sup>4</sup> *Dingl. polyt. J.*, ccxxix., p. 353.

it has been shown by Beilstein and Kurbatoff that this petroleum contains principally hydrogen addition-products of the benzene series, isomeric, but not identical, with the fatty compounds of the series  $C_nH_{2n}$ , it is easily explained how large quantities of benzenoid hydrocarbons could be obtained by the igneous decomposition of that substance.

In that oil-gas tar Letny found :—

	Per cent.	Containing
Water . . . . .	2.3	
Light oil, boiling up to 90° . . . . .	4.6	benzene, toluene, xylene, etc.
"    "    from 90° to 140° . . . . .	5.2	
Middle oils, "    "    140° " 200° . . . . .	1.8	
Heavy oil, "    "    200° " 270° . . . . .	26.9	naphthalene and unchanged petroleum. anthracene, phenanthrene, etc.
Anthracene oil, boiling from 270° to 340° . . . . .	8.6	
"    "    "    above 340° . . . . .	27.6	
Pitch . . . . .	20.6	
Loss . . . . .	2.5	

The specific gravity of this tar was remarkably high, viz. 1.207.

The tar obtained in superheating naphtha residues has also been examined by Dziewonski (*Chem. Rev.*, 1902, p. 36; *Chem. Zeit.*, 1902, p. 492).

In 1879, experiments made at my laboratory on a somewhat large scale by a chemist sent there by one of the largest Russian petroleum refiners (Ragosine), with an apparatus constructed by myself, fully confirmed the fact that large quantities of benzene, toluene, naphthalene, and anthracene could be obtained from petroleum residues in the above-described manner. In 1881, as reported by Rudnew,<sup>1</sup> in fact, the tar from the Kasan gas-works, where petroleum residues form the raw materials for gas-making, was distilled in the ordinary way; it yielded 10 to 12 per cent. of benzol, up to 5 per cent. of naphthalene, and some anthracene, but hardly any phenols.

In 1882, according to Liebermann,<sup>2</sup> the working-up of petroleum residues in the above-described manner was industrially carried out by the brothers Nobel at Baku. The anthracene prepared by them tested 25 to 30 per cent., and at the Ludwigshafen works yielded very good alizarin. The naphthalene was pure. The benzol, although boiling at 80° to 85°, was

<sup>1</sup> *Dingl. polyt. J.*, cccxxix., p. 72.

<sup>2</sup> *Ibid.*, cclvi., p. 429; *J. Soc. Chem. Ind.*, 1883, p. 128.

unsuitable for nitrobenzol, as it contained too many fatty hydrocarbons; but it can be easily purified by freezing at  $-14^{\circ}$  (a process easily practicable in Russia during winter), even when containing 30 per cent. of impurities, and thus made to yield pure nitrobenzene, boiling at  $205^{\circ}$ . The naphtha residues are dropped into red-hot iron retorts filled with pumice; they yielded, per 1000 kg., 500 cbm. (= 17,650 cub. ft.) of gas, employed for heating and lighting, together with 300 kg. of tar, containing 0.6 per cent. of crude anthracene and 17 per cent. of crude benzol (boiling at  $120^{\circ}$ , and, indeed, containing only about 4 or 5 per cent. of benzene and toluene).

In the year 1882 there were produced at Baku 200,000 tons of naphtha residues, which were sold as fuel for steamboats, etc., and for the manufacture of gas in Russia; but only a very small proportion of this was worked for benzol and anthracene. The outlay for plant is extremely large. Kraemer found that, employing pipes 5 to 6 in. wide and 7 to 9 ft. long, two set in one furnace, no more than 2 cwt. of residues could be passed through in 24 hours. By his mode of purification he was able to prepare oils containing 91 or even 96 per cent. of nitrifiable benzol; while Liebermann's method yielded to him only oils containing 24 per cent. of nitrifiable benzol.

Statements concerning the Russian trials of employing petroleum residues ("astatki") as sources of benzene, naphthalene, and anthracene, have been made by B. Redwood (*J. Soc. Chem. Ind.*, 1885, p. 79), from observations made during a visit to Baku in 1884. He mentions a "cupola regenerative furnace" patented by Nobel, and quotes the following details obtained from that gentleman. The first treatment gives 30 to 40 per cent. of tar, containing 15 to 17 per cent. of 50 per cent. benzol. By a second destructive distillation of heavy oils remaining in the tar after the separation of the benzol, 70 per cent. of tar is obtained, containing from 7 to 10 per cent. of 50 per cent. benzol, 16 per cent. of naphthalene, 2 or 3 per cent. of dry "green grease" (containing 30 per cent. anthracene), and 24 per cent. of pitch. There is also obtained in the process per cubic foot of astatki, 75 to 100 cub. ft. of gas, having an illuminating power five times greater than that of coal-gas. The regenerative furnace is first heated to  $1000^{\circ}$  C. (astatki being, of course, the heating-agent), and after having become cooled during the pro-

cess of decomposing the astatki, it is again similarly heated, the gas remaining in the furnace and the coke deposited on the hearth being utilized as fuel. The furnace is stated to remain in working order without cleaning for twelve months. The progress, in spite of being carried out on a somewhat large scale, had evidently not passed beyond the experimental stage, and has no doubt been stopped since Redwood's visit, owing to a fall in prices. Engler, who visited the same district in 1885, reports nothing of it.

Another trial of the same method was made in the United States by a Swiss chemist, who had seen something of the experiments made in my Zurich laboratory; but although a good deal of capital was sunk in the enterprise, the result was most unsatisfactory, either owing to that chemist's inexperience or to the adverse nature of American petroleum residues, which do not seem to have the same composition as the similar material obtained in the Caucasus.

Hlawaty (*Chem. Ind.*, 1891, p. 69; Ger. P. 51553) passes strongly superheated steam into a mixture of petroleum residue, etc., with one-third sawdust and one-sixth quicklime. The vapours are passed through red-hot pipes filled with iron or carbon, and are then subjected to condensation. The liquid obtained contains much aromatic hydrocarbons; the gases consist mostly of acetylenes, and, after passing through a purifying mixture of lime, copperas, and sawdust, they are conducted through red-hot pipes filled with pumice, where they furnish another aromatic condensate. In lieu of steam, the superheated vapours from ethyl or methyl-alcohol or acetic acid may be employed.

Boissieu (*Chem. Zeit.*, 1893, p. 70) found that Russian "massud" (petroleum residue), differently from shale oil or American petroleum, furnishes 12 to 15 per cent. aromatic products by dry distillation. According to him, this quantity would be increased by employing extreme cold and compression in the condensers. The crude benzol thus obtained yielded 69 per cent. at 100°, 96 per cent. at 140°, and the total yield was 8.04 per cent. benzene, 2.57 per cent. toluene, and 1.05 per cent. xylenes. The aniline and toluidine made therefrom were of excellent quality.

Nikiforow (B. Ps. 19957, 1886, and 21374, 1901; Russian

P. 290, of 1904; Ger. P. 85884, of 1905) splits up the residues into fractions by strong heat applied under pressure. They are first vaporized under ordinary pressure in a semi-oval cast-iron retort at  $515^{\circ}$  to  $550^{\circ}$ . The receiver is kept at  $200^{\circ}$ , so that only high-boiling products are here condensed, which are either burnt underneath the retorts, together with the permanent gases, or again subjected to decomposition. The vapours issuing from the first receiver are cooled down in a worm, and the condensing liquid is distilled in ordinary tar-stills provided with reflux-coolers. The fractions up to  $100^{\circ}$ ,  $130^{\circ}$ ,  $160^{\circ}$ ,  $180^{\circ}$ , and  $200^{\circ}$  are separately condensed; the residue is used, like the tar, from the first receiver. Each fraction is separately treated in an oil-gas retort, two of which are always combined; they are here decomposed at temperatures varying from  $700^{\circ}$  for the lightest to  $1200^{\circ}$  for the heaviest fraction, under a pressure of two atmospheres. The first receiver is kept at  $150^{\circ}$  or  $200^{\circ}$ ; the vapours uncondensed here are condensed by cooling, fractionally distilled, and aniline-benzol recovered from the fraction boiling up to  $120^{\circ}$ . The fractions up to  $160^{\circ}$ ,  $180^{\circ}$ , and  $200^{\circ}$  re-enter the cycle of operations; those above  $200^{\circ}$  are worked for naphthalene and anthracene. The tar collected in the first vaporization may be dealt with in a similar manner, treating the fractions at much higher temperatures under pressure, but yields much less aromatic hydrocarbons. The total yield of these is about 12 per cent. Nikiforow's process has been carried out on a large scale at Kineshma, in Russia, employing high temperature and pressure. By the first distillation of the naphtha or naphtha residues, 38 per cent. tar is obtained, half of it consisting of aromatic hydrocarbons. At the second distillation these are obtained in a sufficiently pure state, the yield being 12 per cent. benzene and toluene, 2 or 3 per cent. naphthalene, 1 per cent. anthracene. The German patent, No. 143549, awarded for this process, was cancelled a few years after, and the manufacture in Russia was stopped after a fire. The cost of the benzol obtained by this process was 1.06 mark per kilogram—that is, four or five times that of English benzol. A favourable report on Nikiforow's process was made by Oglobine (*Z. angew. Chem.*, 1905, p. 406), but the stoppage of the factory proves that it did not pay.

Later on Nikiforow took out a British patent, No. 17450, of 1907, for the following process. Hydrocarbons of a boiling-point not exceeding  $200^{\circ}\text{C}$ ., obtained by the destructive distillation of naphtha, are pulverised by directing a current of water-gas, issuing from a suitable nozzle against a jet of the oil previously heated to  $200^{\circ}\text{C}$ ., and the mixture is caused to pass through a retort. The water-gas is previously heated in a coil to a temperature of  $800^{\circ}$  to  $1000^{\circ}\text{C}$ ., and to keep up the heat more water-gas of the same temperature is introduced into the retort at both ends. By this means aromatic hydrocarbons are formed which collect together with soot in a catch-box provided with a stirring-arrangement, whilst the gases and uncondensed hydrocarbons escape. The condensed hydrocarbons are drawn off through an overflow, and when working at  $800^{\circ}$  to  $850^{\circ}\text{C}$ ., the products are stated to be: 15 per cent. of commercial benzol, 4 per cent. of naphthalene, 0.5 per cent. of anthracene, 10 to 12 per cent. of coke, 9 per cent. of coked material and soot, and 50 per cent. of gas of 14 candles illuminating power.

Dvorkovitch (B. P. 21647, 1892; *J. Gas Lighting*, 1893, ii. p. 1083) has constructed an apparatus on the lines laid down by Young (p. 185), which has been erected at Ragosine's works at Nischni-Novgorod, and is stated to yield 40 kl. 50 per cent. benzol from 100 kl. petroleum. One hundred kilolitres of Russian petroleum yield 46.7 cbm. gas of 60.3 standard candles, with an hourly consumption of 150 litres, and 37 per cent. tar. The latter yields: 32.4 per cent. benzol, 41.1 per cent. light oil, 0.14 per cent. anthracene, 11 per cent. pitch, and 11 per cent. lubricating oil.

Wisse and Schneller (B. P. 21343, 1892) propose employing an electrically heated furnace for the decomposition of these residues. Seigle (*J. Gas Lighting*, 1893, ii. p. 629) employs a lead bath. Another furnace for a similar purpose has been constructed by Meffert (Ger. P. 99254).

Hausmann and Pilat (Ger. P. 227178, 1909) pass the vapours of petroleum or petroleum fractions into highly heated tubes, filled with contact bodies, consisting of metallic oxides, peroxides, and salts, such as manganese peroxide, ferric sulphate, calcium permanganate, etc., which transfer the oxygen of the air passed into the tubes to the hydrogen carbides of the petroleum, and dispense with the employment of aqueous vapour. It is asserted

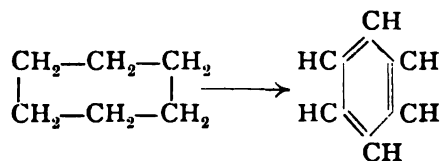


that 90 per cent. of the oils employed, or even more than that, is thus converted into aromatic hydrocarbons.

Starke (U.S. P. 913780) treats the "distillate of petroleum which contains a benzene nucleus," by agitating and heating with concentrated sulphuric acid, until the evolution of sulphur dioxide ceases. The mass is then allowed to settle until the sulphonic acids have separated from the petroleum, and the benzene is recovered from the sulphonic acids by distillation.

All these proposals have at the present day hardly more than scientific interest. On the one hand, it is now known that petroleum residues can be converted into valuable lubricating oils and asphalt; on the other hand, there is no lack of products from coal-tar, and no necessity to produce similar substances in such a roundabout way. For the same reason the proposals of Dvorkovitch, referring to the manufacture of gas, in which the loss of gas and illuminating power is to be compensated by the value of benzol, etc. (p. 193), have been adversely criticised by Scheithauer (*loc. cit.*) and Lewes (*J. Gas Lighting*, 1893, ii, p. 619).

The view has been uttered that the production of aromatic hydrocarbons from petroleum residues, etc., is owing to the decomposition of the naphthenes present, and especially the close connection between hexanaphthene and benzene has been pointed out:



If this were the case, success would mostly depend upon the proportion of naphthenes in the residues worked, which, perhaps, is less favourable in the American petroleum than in that from Caucasia.

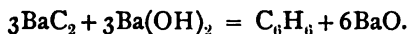
In *Chem. Ind.*, 1915, p. 201, Pietrusky reports that Dr W. F. Rittmann, of the U.S. Bureau of Mines, on 8th March 1915 demonstrated a "new" process for obtaining from mineral oils, benzene and toluene, together with an increased yield of benzin. It would appear that this process consists in passing the oil through an iron tube, heating it therein to upwards of

450° under a pressure of about 90 lb. per superficial inch, where the object is the production of benzin. If the temperature is raised to 500°, and the pressure to 100 lb. per superficial inch, benzene and toluene are obtained. The Bureau of Mines has made a contract with the Etna Explosives Co. for working out the technical details of this process, and it has erected a factory for this purpose at Pittsburg. Details are only to be published after the patents demanded by the Bureau of Mines have been granted. (Pietrusky remarks that it is questionable whether such patents will be granted, as the production of aromatic hydrocarbons from mineral oils has been known for nearly forty years. It is, however, possible that the above-mentioned process contains novel features which are patentable.)

If at any time petroleum can come into question as a source of aromatic hydrocarbons for the manufacture of colours, this cannot be done, at the present situation of the market, by aromatizing the aliphatic petroleum hydrocarbons. Of greater importance is the fact that by the petroleum industry of Japan, Borneo, Sumatra, and Java, benzines containing a considerable proportion of benzol and toluol are imported at a moderate duty, which may lead to very sharp competition with the German benzol industry for the manufacture of colours and motor-engines.

*G. Synthetic Production of Aromatic Hydrocarbons by Means of Barium Carbide.*

Bradley and Jacobs (Ger. P. 125936) heat barium carbide with barium or sodium hydrate at 600° to 1200° C., whereby benzol, naphthalene, and anthracene are formed according to the equation (for benzene):



The yield is stated to be very good, but at the present low prices of those products there is hardly any chance for this process.

*General Observations on Coal-tar from Various Sources.*

All the above-mentioned varieties of coal-tar, to which we might add natural tars—as the Rangoon naphtha and, in a

wider sense, even crude petroleum—are principally (although never exclusively) composed of hydrocarbons; but these belong to very different classes, and the members of these classes are present in various proportions. In some of them the “*aromatic*” hydrocarbons—that is, those belonging to the benzene series in its widest sense—are altogether predominant; and these “*benzenoid*” tars are those which yield the raw material for the manufacture of coal-tar colours—benzene, toluene, xylene, naphthalene, anthracene, and carbolic acid. In other tars, which we call the “*paraffinoid*” tars, we find, apart from phenols of higher orders, the members of the paraffin series and others closely related to it, as the olefines, all of them belonging to the “*aliphatic*” or “*fatty*” compounds. Some of these tars are stated to contain compounds which, although isomeric with paraffins or olefines, are yet in reality aromatic compounds namely, hydrogen addition-products (*cf.* next chapter); but this does not seem to make any practical difference in the way in which such tars can be utilized (that is, merely for the manufacture of burning and lubricating oils and of solid paraffin), while they are useless for the manufacture of coal-tar colours.

As a rule, the members of both series are found to a certain extent in all kinds of tar; and this is a rule without exception, if we include the phenols, which are all “*aromatic*” compounds, and which do not seem to be ever absent in any coal-tar. Those tars are most valuable which contain most benzenoid hydrocarbons; even a rather small proportion of paraffinoid hydrocarbons greatly lessens their value for colour-making, and any considerable admixture of such may make them practically worthless for that purpose. Benzol which contains many “*unnitriifiable*” oils is not accepted by any aniline manufacturer; and anthracene containing paraffin is dreaded by every alizarin maker. Hence the practical value of some of the tar-producing processes described above is very questionable, since they yield a mixture of benzenoid and paraffinoid compounds containing too much of the latter kind. It is of course not impossible that good and cheap manufacturing methods will be found for separating these two kinds of compounds; but until that is the case, those processes have no chance of competing with gas-tar and with some descriptions of coke-oven tars.

It is, of course, an important question : What are the conditions under which the formation of benzenoid or that of paraffinoid compounds predominates? We have already seen (pp. 38 *et seq.*) that differences of temperature have a great deal to do with it; but this does not account for everything. Without doubt the physical condition and the chemical composition of the coal distilled are of great importance: older fossils yield more benzenoid hydrocarbons, younger ones more paraffins and phenols (p. 49). But even when treating one and the same material, ordinary gas-coal or coking-coal, great differences are observed according to the method of applying the heat. We will illustrate this by the following quotation from a paper by Watson Smith (*Industries*, 1886, p. 139):—

“In the cases in which the benzenoid tars (those useful for coal-tar colours) are yielded, the condition which must be observed is an intense heat applied to a relatively thin layer of the fuel. If this condition be not observed, consecutive distillation occurs, in which, in the interior of the mass of coal (a comparatively bad conductor of heat), or in that part of the oven or retort in which the heat is less intense, products of the paraffinoid class mainly are first distilled at the lower temperature there existing, pass outwards to the exterior, and escape in such abundance into the highly heated oven or retort space, and thence are so rapidly drawn off to the condensing arrangements that a large proportion of the paraffinoid matters still predominate in the product condensed.

“In the other case, however, in which the layer of fuel is sufficiently thin, sufficiently exposed on all sides to the intense heat, as fast as the constituents of the coal rearrange themselves to form the products at all, they do so almost directly to form the high-temperature products and benzenoid constituents, and the consecutive is almost entirely merged in a more or less direct process.

“The truth of these observations is well illustrated in the forms, mode of heating, and general arrangement of the ordinary gas-retorts, and in the Simon-Carvès coke-ovens, and, in opposition to them, the Jameson's adapted beehive coke-ovens, where the coal lies in a dense mass spread out on the floor of the same, which is not heated below; nor are the sides heated, but the heat is applied to the upper surface of the carbonizing fuel.

Also, in another form of the adapted beehive coke-oven the coal lies in a dense mass on the floor, which is heated strongly by flues passing below the floor or bed; but neither sides nor top are heated, and if the top were heated there would be too great a space between it and the fuel. In both the latter cases, paraffinoid tars are produced."

To this we need only add that the same conditions as exist in the case of gas-retorts and Simon-Carvès coke-ovens for producing benzenoid tars are offered by the Otto coke-ovens and other similar forms; while the conditions for the predominance of paraffinoid compounds are also furnished as a natural consequence of their mode of action, by gas-producers and blast-furnaces working with coal.

#### *Determination of the Yield of Tar and Ammonia from Coal.*

It is, of course, desirable to know beforehand what quantity of tar and ammonia a new description of coal may be expected to yield. Such estimations would certainly be far more important if tar and ammonia ever became the principal products of the distillation of coal; but we have seen above that this state of affairs, which at one time seemed to be approaching, is now once more relegated to a distant future. Under present circumstances the quantity and quality of the gas and the coke obtained in distillation are decidedly the primary considerations.

Nevertheless it occasionally happens that either coal-owners or coal-consumers wish to enlighten themselves as to the yield of by-products from some special description of coal. Hitherto the only reliable means of arriving at that result has been to distil some truck-loads of coal in the same retorts or ovens which are used for the ordinary manufacture, taking care that the by-products are separately collected. This is not very easy, especially so far as the tar is concerned, since there is always a good deal remaining from previous operations in the hydraulic main, etc.; but it can be done by special care, and we have already noticed (pp. 58 *et seq.*) such experiments performed at Paris.

This test is, of course, not always possible to perform, and it is very desirable to arrive at the yield of by-products by a

test on the laboratory scale. Instead, however, of describing any apparatus or process for this purpose, I will point out the difficulties of such testings. At the very least there should be provided an experimental retort, imitating the conditions on the large scale as closely as possible; for instance, a small cast-iron D-shaped retort, 18 in. long and 6 in. high (inside measurement), with a head, cover, and gas-delivery tube similar to those of ordinary gas-retorts, in which about 10 lb. of coal can be distilled. Even here the conditions are very different from those of a real gas-retort; and we must expect to get a very different quantity of tar, and of quite different quality, from that which the same coal will produce in a full-sized fireclay gas-retort or a coke-oven. In the case of ammonia, also, the distillation on the small scale is no guide as to that on the large scale. It is, of course, utterly hopeless to expect anything like trustworthy results when chemists work with even smaller apparatus, such as glass combustion-tubing, porcelain tubes, or gun-barrels. S. Schmitz<sup>1</sup> believes he can obtain good results in testing for ammonia by passing the gases evolved in distilling 10 or 15 g. of coal in a combustion-tube over red-hot coke contained in the first half of the tube; but here it is uncertain how much of the ammonia is derived from the coal distilled, and how much from the action of the gases and vapours on the coke, which always contains nitrogen. The gases are absorbed in dilute sulphuric acid, the liquid evaporated to a small volume with the addition of oxide of mercury, and the ammonia driven off by caustic soda. This method will at best allow comparative results to be obtained for different kinds of coal, but it cannot be expected that these results will coincide with manufacturing practice.

<sup>1</sup> *Stahl u. Eisen*, 1886, p. 396.

## CHAPTER III

### THE PROPERTIES OF COAL-TAR AND ITS CONSTITUENTS

COAL-TAR is a black, more or less viscid fluid of peculiar smell, of specific gravity 1.1 to 1.28, usually between 1.12 and 1.15; London tar averages 1.2, and sometimes amounts to 1.215; country tars are lighter; cannel-coal tars still more so.<sup>1</sup> It has been asserted by some that tar is more valuable the lower its specific gravity. In any case, this could only be said of pure coal-tar, whose specific gravity generally rises with its contents of free carbon; but since the tar from cannel-coal, shale, etc., which contains more toluene and paraffin than coal-tar, is much lighter than the latter, the above criterion is not in any way to be depended upon.

The determination of the specific gravity of tar, tar-oils, and pitch is described by J. M. Weiss (*J. Ind. Eng. Chem.*, vii., p. 21), according to well-known methods.

Coal-tar, like some of its constituents, has *poisonous* properties. Even on the surface of the skin it sometimes causes inflammation. The reports of the British factory inspectors repeatedly mention this, and consider it identical with the "chimney-sweeps' itch." Workmen who take regard to cleanliness are never visited by such complaints, which have never been observed in the case of men occupied in the department of crude tar, but now and then on men employed in the anthracene and pitch department. Broex (*Monatshefte für prakt. Dermatologie*, 1909, p. 267), on the other hand, reports on the curative effects of tar in external use in certain skin diseases

<sup>1</sup> It is strange that authors like Bolley, Wurtz, Girard and Delaire, Vincent, and others have stated the specific gravity of coal-tar to be equal to or below that of water. Evidently there has been confusion with tar from browncoal or boghead, etc.; and a wrong quotation of this kind has passed from one book to another without criticism.

(eczemas). According to the Report of the Baden Factory Inspectors for 1906 and 1907 (*Chem. Ind.*, 1907, pp. 24 and 364), chlorinated tar-compounds are assumed to cause these phenomena.

According to H. W. Robinson's B. P. 20767, of 1913, the properties which render coal-tar or the products obtained therefrom likely to produce "pitch cancer" are reduced or removed by treating the tar before distillation, or at some stage during the distillation, during which the distillation is suspended, with ozonized air, with or without steam.

Coal-tar is an extremely complex mixture of chemical compounds, some of which have not yet been even isolated. Thus comparatively little is known of the indifferent oils occurring in its distillation, between the phenols and naphthalene on the one hand, and anthracene oil on the other; neither do we know all the compounds existing in crude anthracene, and still less those constituting the pitch, but considerable progress has been made in this direction during recent times. Whether some of the constituents of coal-tar are already present in the coal, and are therefore simply evolved by the ordinary process of distillation, must be left an open question. It can hardly be doubted that coal contains aromatic compounds; probably it is entirely made up of such, and contains no really free carbon at all. But it is another question whether any of these compounds are volatile, without change, at the temperature existing in the gas-retorts.

Tar contains nitrogenous compounds, chiefly of a basic nature, owing to the nitrogen always found in the coal, and sulphur compounds, derived from the pyrites, etc., are never absent in coal.

E. J. Mills (*J. Soc. Chem. Ind.*, 1885, p. 326) gives the following ultimate analyses of London and of average Scotch canal gas-tar:—

		London.	Scotch canal.
Carbon	.	77.53	85.33
Hydrogen	.	6.33	7.33
Nitrogen	.	1.03	0.85
Sulphur	.	0.61	0.43
Oxygen	.	14.50	6.06
		<u>100.00</u>	<u>100.00</u>

Kraemer (*J. Gasbeleucht.*, 1891, p. 225) makes the following



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statements about the composition of German gas-tars obtained at that time:—

Benzol and its homologues, $C_nH_{2n-6}$ . . .	2.50 per cent.
Phenols and homologues, $C_nH_{2n-7}.OH$ . . .	2.00 "
Pyridine and Quinoline bases, $C_nH_{2n-7}.N$ . . .	0.25 "
Naphthalene (Acenaphthene) $C_nH_{2n-12}$ . . .	6.00 "
Heavy oils, $C_nH_n$ . . .	20.00 "
Anthracene, Phenanthrene, $C_nH_{2n-8}$ . . .	2.00 "
Asphalt (soluble constituents of pitch), $C_{2n}H_n$ . . .	38.00 "
Coal (insoluble constituents of pitch), $C_{8n}H_n$ . . .	24.00 "
Water . . .	4.00 "
Gases and loss in distillation . . .	1.25 "

### *Enumeration of the Compounds contained in Coal-tar.*

Since tar always contains a considerable quantity of ammoniacal liquor mechanically mixed with it, we must expect to find all the constituents of the latter in the tar; also all those of the gas probably occur in the tar, being absorbed by it.

The following is an enumeration of the compounds hitherto found in coal-tar or reasonably presumed to exist in it; they will subsequently be described in detail:—

	Formula.	Melting-point.	Boiling-point.
<b>A. HYDROCARBONS.</b>			
<b>I. Methane Series, <math>C_nH_{2n+2}</math>.</b>			
Methane . . . . .	$CH_4$		
Ethane . . . . .	$C_2H_6$		
Propane . . . . .	$C_3H_8$		
Butane (normal) . . . . .	$C_4H_{10}$	...	+1
Pentane (normal) . . . . .	$C_5H_{12}$	liquid	37-39
Isopentane . . . . .	$C_5H_{12}$	"	30
Hexane (normal) . . . . .	$C_6H_{14}$	"	69-71
Heptane (normal) . . . . .	$C_7H_{16}$	"	98
Ethylisoamyl . . . . .	$C_7H_{16}$	"	90-3
Octane, I. . . . .	$C_8H_{18}$	"	119-120
" II. . . . .	$C_8H_{18}$	"	124
Nonane, I. . . . .	$C_9H_{20}$	"	130
" II. . . . .	$C_9H_{20}$	"	150-8
Decane, I. . . . .	$C_{10}H_{22}$	"	158-161
" II. . . . .	$C_{10}H_{22}$	"	170-171
Undecane . . . . .	$C_{11}H_{24}$	"	180-182
Duodecane . . . . .	$C_{12}H_{26}$	"	200-202
Tredecane . . . . .	$C_{13}H_{28}$	"	218-220
Quatuordecane . . . . .	$C_{14}H_{30}$	"	236-240
Quindecane . . . . .	$C_{15}H_{32}$	"	258-262
Sedecane . . . . .	$C_{16}H_{34}$	"	280
Solid Paraffins . . . . .	$\left\{ \begin{array}{l} C_{17}H_{36} \\ \text{to} \\ C_{27}H_{56} \end{array} \right\}$	40-60	

	Formula.	Melting-point.	Boiling-point.
A. HYDROCARBONS ( <i>continued</i> )			
° C.			
II. Ethylene Series, $C_nH_{2n}$ .			
Ethylene . . . . .	$C_2H_4$	...	-110
Propylene . . . . .	$C_3H_6$	...	
Butylene (normal) . . . . .	$C_4H_8$	...	-5
Pseudobutylene . . . . .	$C_4H_8$	...	+1
Isobutylene . . . . .	$C_4H_8$	...	-8
Amylene (normal) . . . . .	$C_5H_{10}$	liquid	39-40
Isoamylene . . . . .	$C_5H_{10}$	"	35-36
Hexylene . . . . .	$C_6H_{12}$	"	68-70
Isohexylene . . . . .	$C_6H_{12}$	"	72-74
Heptylene . . . . .	$C_7H_{14}$	"	96-99
III. Hexahydro - Addition - products of the Benzene Series, $C_nH_{2n}$ (Naphthenes, Paraffenes).			
Hexahydrobenzene . . . . .	$C_6H_{12}$	liquid	69
Hexahydrotoluene . . . . .	$C_7H_{14}$	"	97
Hexahydroisoxylene . . . . .	$C_8H_{16}$	"	118
IV. Acetylene Series, $C_nH_{2n-2}$ .			
Acetylene . . . . .	$C_2H_2$		
Allylene . . . . .	$C_3H_4$		
1-3 Butadiene . . . . .	$C_4H_6$		
Crotonylene . . . . .	$C_4H_6$	liquid	18
Valylene (Piperylene) . . . . .	$C_5H_8$	"	41-42
Hexoylene . . . . .	$C_6H_{10}$	"	80
Higher members . . . . .	$C_{12}H_{20}$	"	210
" " . . . . .	$C_{14}H_{24}$	"	240
" " . . . . .	$C_{16}H_{28}$	"	280
V. Tetrahydro - Addition - products of the Benzene Series, $C_nH_{2n-2}$ (Naphthylenes).			
Tetrahydrobenzene . . . . .	$C_6H_{10}$	liquid	82
Tetrahydrotoluene . . . . .	$C_7H_{12}$	"	103-105
Tetrahydroxylene . . . . .	$C_8H_{14}$	"	129-132
VI. Series $C_nH_{2n-4}$ .			
Cyclopentadiene . . . . .	$C_5H_6$	liquid	42.5
Nonene . . . . .	$C_9H_{14}$	"	174
VII. Aromatic Dihydro-Addition-products, $C_nH_{2n-4}$ (Terpenes).			
Dihydrobenzene . . . . .	$C_6H_8$	liquid	81.5
Dihydrotoluene . . . . .	$C_7H_{10}$	"	105-108
Dihydroxylene . . . . .	$C_8H_{12}$	"	132-134
Dihydrocymene . . . . .	$C_{10}H_{16}$	"	174

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	Formula.	Melting-point.	Boiling-point.
A. HYDROCARBONS ( <i>continued</i> )			
° C.			
VIII. Benzene Series, $C_nH_{2n-6}$			
Benzene . . . . .	$C_6H_6$	5.5	80.5
Toluene . . . . .	$C_7H_8$	liquid	111
Xylene . . . . .	$C_8H_{10}$	"	"
Orthoxylene . . . . .	...	"	142
Metaxylene . . . . .	...	"	139
Paraxylene . . . . .	...	15	138.5
Pseudocumene . . . . .	$C_9H_{12}$	liquid	169.8
Mesitylene . . . . .	$C_9H_{12}$	"	164.5
Hemellithol . . . . .	$C_9H_{12}$	"	175
Ethylbenzene . . . . .	$C_8H_{10}$	"	137
Propylbenzene (Cumene) . . . . .	$C_9H_{12}$	"	...
Ethyltoluenes . . . . .	$C_9H_{12}$	"	168
Cymene . . . . .	$C_{10}H_{14}$	"	180
Durene . . . . .	$C_{10}H_{14}$	80-81	196
Other tetramethylbenzenes . . . . .	...	...	...
IX. Naphthenes.			
X. Styrolene (?), $C_nH_{2n-8}$			
Hydride of styrolene (?) . . . . .	$C_8H_8$	liquid	145
	$C_8H_{10}$	"	"
XI. Indene, $C_nH_{2n-10}$			
Hydrindene . . . . .	$C_9H_8$	"	182
Methylindene . . . . .	$C_9H_{10}$	"	176
Dimethylindene . . . . .	$C_{10}H_{10}$	"	195-200
	$C_{11}H_{12}$	"	...
XIa. Dicyclopentadiene . . . . .			
	$C_{10}H_{12}$	40.5	170
XII. Naphthalene, $C_nH_{2n-12}$			
Naphthalene . . . . .	$C_{10}H_8$	79.8	218
Naphthalene dihydride . . . . .	$C_{10}H_{10}$	liquid	200-210
" tetrahydride . . . . .	$C_{10}H_{12}$	"	190
$\alpha$ Methylnaphthalene . . . . .	$C_{11}H_{10}$	"	240-243
$\beta$ Methylnaphthalene . . . . .	$C_{11}H_{10}$	32.5	241-242
Dimethylnaphthalene . . . . .	$C_{12}H_{12}$	liquid	262-264
Phenylnaphthalenes (?) . . . . .	$C_{16}H_{12}$		
XIII. Acenaphthene, $C_nH_{2n-14}$			
Acenaphthene hydride . . . . .	$C_{12}H_{10}$	95	278
Diphenyl . . . . .	$C_{12}H_{12}$	...	260
	$C_{12}H_{10}$	70.5	254
XIV. Fluorene, $C_nH_{2n-16}$			
	$C_{13}H_{10}$	116	295
XV. Anthracene, $C_nH_{2n-18}$			
Anthracene . . . . .	$C_{14}H_{10}$	216.5	360
Anthracene dihydride . . . . .	$C_{14}H_{12}$	106	305
" hexahydride . . . . .	$C_{14}H_{16}$	63	290
" perhydride . . . . .	$C_{14}H_{24}$	88	250
Methylanthracene . . . . .	$C_{15}H_{12}$	208-210	above 360
Isomethylanthracene . . . . .	$C_{15}H_{12}$	202-204	
Dimethylanthracene (?) . . . . .	$C_{16}H_{14}$	224-225	

	Formula.	Melting-point.	Boiling-point.
		° C.	° C.
<b>A. HYDROCARBONS (continued)</b>			
<b>XV. Anthracene (continued)</b>			
Phenanthrene . . . . .	$C_{14}H_{10}$	96	340
Pseudophenanthrene . . . . .	$C_{16}H_{12}$	115	above 360
Synanthrene . . . . .	$C_{14}H_{10}$	189-195	
Fluoranthene . . . . .	$C_{15}H_{10}$	109	above 360
Pyrene . . . . .	$C_{16}H_{10}$	148	above 360
Chrysene . . . . .	$C_{18}H_{12}$	250	436
Chrysene hydride . . . . .	$C_{18}H_{28}$	liquid	360
Chrysene perhydride . . . . .	$C_{18}H_{30}$	115°	353
Chrysogene . . . . .	...	280-290	
Retene . . . . .	$C_{18}H_{18}$	98-99°	350
Retene dodecahydride . . . . .	$C_{18}H_{30}$	liquid	336
Succisterene (?) . . . . .	...	160-162	above 300
Picene . . . . .	$C_{22}H_{14}$	364	518-520
Picene eikosihydride . . . . .	$C_{22}H_{34}$	liquid	360
Picene perhydride . . . . .	$C_{22}H_{36}$	175	360
Benzerythrene . . . . .	$C_{24}H_{18}$	307-308	
Crackene . . . . .	$C_{24}H_{18}$	308	over 500
Bitumene . . . . .	...	...	...
Truxene . . . . .	$C_{27}H_{18}$	365	...
<b>B. OXYGENIZED COMPOUNDS.</b>			
Water . . . . .	$H_2O$	0	100
Methylic alcohol (?) . . . . .	$CH_3O$	liquid	63
Ethylic alcohol (?) . . . . .	$C_2H_5O$	"	78.5
Acetone . . . . .	$C_3H_6O$	"	56
Ethylmethyl ketone (?) . . . . .	$C_4H_8O$	"	77.5-81
<b>Acids and Phenols.</b>			
Acetic acid . . . . .	$C_2H_4O_2$	16	119
Benzoic acid . . . . .	$C_7H_6O_2$	121	249
Phenol (carbolic acid) . . . . .	$C_6H_6O$	42	184
Orthocresol . . . . .	$C_7H_8O$	30	191
Paracresol . . . . .	"	36.5	202
Metacresol . . . . .	"	3-4	203
Xylenols: Ortho 1, 2, 4 . . . . .	$C_8H_{10}O$	61	225
Meta 1, 2, 3 . . . . .	"	73	216
Meta 1, 3, 4 . . . . .	"	26	211.5
Para 1, 3, 4 . . . . .	"	74.5	211-213
$\alpha$ Naphthol . . . . .	$C_{10}H_8O$	94-96	280
$\beta$ Naphthol . . . . .	"	122	294
Phenols of the Anthracene series (?) . . . . .	"	?	
$\alpha$ Pyrocresol . . . . .	$C_{18}H_{14}O$	196	350
$\beta$ Pyrocresol . . . . .	"	124	
$\gamma$ Pyrocresol . . . . .	"	105	
Rosolic acid (?) . . . . .	$C_{18}H_{14}O_3$		
Brunolic acid (?) . . . . .			
Cumarone . . . . .	$C_9H_8O$	liquid	169
$p$ -methyl-cumarone . . . . .	$C_9H_8O$	"	197-199
$m$ -methyl-cumarone . . . . .	"	"	195-196
$o$ -methyl-cumarone . . . . .	"	"	190-191
$o,p$ -dimethyl-cumarone . . . . .	$C_{10}H_{10}$	"	221-222
$m,p$ -dimethyl-cumarone . . . . .	"	"	221
$o,m$ -dimethyl-cumarone . . . . .	"	"	216

## 206 PROPERTIES OF COAL-TAR AND ITS CONSTITUENTS

	Formula.	Melting-point.	Boiling-point.
B. OXYGENIZED COMPOUNDS ( <i>con.</i> )			
<i>Acids and Phenols (continued)</i>			
Trimethyl-cumarone . . . . .	$C_{11}H_{12}$	180°	236
$\beta$ -ethyl-cumarone . . . . .	$C_{10}H_{10}O$	liquid	218
$\alpha$ Naphthofuran . . . . .	$C_{12}H_8O$	"	282-284
$\beta$ Naphthofuran . . . . .	$C_{12}H_8O$	50-51°	284-286
Ciphenylene oxide . . . . .	$C_{12}H_8O$	86	276
Dioxydiphenyl . . . . .	$C_{12}H_{10}O_2$	109	325
Xanthene (?) . . . . .	$C_{13}H_{10}O$		
C. SULPHURETTED COMPOUNDS.			
Hydrogen sulphide . . . . .	$H_2S$		
Ammonium sulphide . . . . .	$(NH_4)_2S$		
" sulphocyanide . . . . .	$(NH_4)NCS$		
Sulphur dioxide . . . . .	$SO_2$		
Carbon bisulphide . . . . .	$CS_2$	liquid	47
" oxysulphide . . . . .	$COS$		
Mercaptanes			
Alliol (?) . . . . .			
Thiophene . . . . .	$C_4H_4S$	liquid	84
$\alpha$ Thiotolene . . . . .	$C_8H_6S$	"	113
$\beta$ Thiotolene . . . . .	"	"	113
$\alpha$ - $\alpha$ Thioxene . . . . .	$C_6H_8S$	"	135-136
$\alpha$ - $\beta$ Thioxene . . . . .	"	"	136-137
$\alpha$ - $\beta^1$ Thioxene . . . . .	"	"	137-138
$\beta$ - $\beta$ Thioxene . . . . .	"	"	136-137
$\alpha$ - $\beta$ - $\beta$ Trimethylthiophene . . . . .	$C_8H_{10}S$	"	163
Tetramethylthiophene . . . . .	$C_6H_{12}S$	"	182-184
Biophen . . . . .	$C_8H_4S_2$	"	165-170
$\alpha^1$ - $\alpha$ Dithienyl . . . . .	$C_8H_6S_2$	33	
$\beta^1$ - $\beta$ Dithienyl . . . . .	"	132.4	
Trithienyl . . . . .	$C_{12}H_8S_3$	147	357
Thionaphthene . . . . .	$C_8H_6S$	30-31	220-221
Thiophthene . . . . .	$C_8H_4S_2$	liquid	224-226
Diphenylene sulphide . . . . .	$C_{12}H_8S$	?	?
D. CHLORINATED COMPOUNDS.			
Ammonium chloride . . . . .	$NH_4Cl$		
E. NITROGENIZED COMPOUNDS.			
I. Basic.			
Ammonia . . . . .	$NH_3$		
(Ammonium compounds mentioned under C, D, & E II.) . . . . .			
Methylamine, ethylamine, etc. . . . .	...	liquid	
Cespite (?) . . . . .	$C_8H_{14}N$	"	95
Aniline . . . . .	$C_6H_7N$	- 8	182
Toluidines (?) . . . . .	$C_7H_9N$	...	197-199
Pyridine . . . . .	$C_5H_5N$	liquid	115
$\alpha$ Picoline . . . . .	$C_6H_7N$	"	133.5
$\beta$ Picoline . . . . .	"	"	143.5
$\gamma$ Picoline . . . . .	"	"	142-144

	Formula.	Melting-point.	Boiling-point.
E. NITROGENIZED COMPOUNDS ( <i>con.</i> )		°C.	°C.
I. <i>Basic</i> (continued)			
αα Lutidine . . . . .	C <sub>7</sub> H <sub>9</sub> N	liquid	142
αβ Lutidine . . . . .	"	"	162-163
αγ Lutidine . . . . .	"	"	157
αβ <sub>1</sub> Lutidine . . . . .	"	"	(?)
βγ Lutidine . . . . .	"	"	163.5-164.5
ββ <sub>1</sub> Lutidine . . . . .	"	"	169-170
γ Ethylpyridine . . . . .	"	"	164-166
αγ <sup>α</sup> Collidine . . . . .	C <sub>8</sub> H <sub>11</sub> N	"	171-172
α <sup>1</sup> βγ Collidine . . . . .	"	"	165-168
Parvoline (?) . . . . .	C <sub>9</sub> H <sub>13</sub> N	"	188
αβγβ <sup>1</sup> Tetramethylpyridine . . . . .	"	"	232-234
Coridine (?) . . . . .	C <sub>10</sub> H <sub>15</sub> N	"	211
Rubidine (?) . . . . .	C <sub>11</sub> H <sub>17</sub> N	"	230
Viridine (?) . . . . .	C <sub>12</sub> H <sub>19</sub> N	"	251
Leucoline (Quinoline) . . . . .	C <sub>9</sub> H <sub>7</sub> N	"	239
Isoquinoline . . . . .	C <sub>9</sub> H <sub>7</sub> N	28	236
Chinaldine (α Methylquinoline) . . . . .	C <sub>10</sub> H <sub>9</sub> N	liquid	238-239
Iridoline (γ Methyllepidine) . . . . .	C <sub>10</sub> H <sub>9</sub> N	"	252-257
Cryptidine (Dimethylquinoline) . . . . .	C <sub>11</sub> H <sub>11</sub> N	"	274
Tetracoline (?) . . . . .	"	"	"
Octacoline (?) . . . . .	"	"	"
Acridine . . . . .	C <sub>13</sub> H <sub>9</sub> N	107	above 360
2-Methylacridine . . . . .	C <sub>14</sub> H <sub>11</sub> N	134	"
4-Methylacridine . . . . .	"	88	"
2-4-Dimethylacridine . . . . .	C <sub>15</sub> H <sub>13</sub> N	71	"
Hydroacridine . . . . .	C <sub>13</sub> H <sub>11</sub> N	107	"
II. <i>Not Basic.</i>			
Indol . . . . .	C <sub>8</sub> H <sub>7</sub> N	52	253-254
Pyrrol . . . . .	C <sub>4</sub> H <sub>5</sub> N	liquid	133
Ammonium cyanide . . . . .	CN . NH <sub>4</sub>	"	"
Methylic cyanide (acetonitrile) . . . . .	CH <sub>3</sub> . CN	"	79
Benzonitrile . . . . .	C <sub>6</sub> H <sub>5</sub> CN	"	191
Methylic isocyanide . . . . .	C <sub>6</sub> H <sub>5</sub> N	"	59-6
Carbazol . . . . .	C <sub>12</sub> H <sub>9</sub> N	238	355
Phenyl- α naphthyl-carbazol . . . . .	C <sub>16</sub> H <sub>11</sub> N	225	above 440
Phenyl- β naphthyl-carbazol . . . . .	"	230	"
F. FREE CARBON . . . . .	C <sub>z</sub>		

HYDROCARBONS OF THE METHANE SERIES, C<sub>n</sub>H<sub>2n+2</sub>

These hydrocarbons are sometimes called hydrides of monad radicals—also paraffins, because a mixture of the higher solid members of the series, as obtained in the distillation of shale, etc., had obtained that name from its great resistance to chemical reactions (*parum affinis*). This mixture, however, contains also non-saturated hydrocarbons (olefins).

The compounds of this series are principally formed in the destructive distillation of wood, peat, shale, browncoal, boghead, cannel-coal, etc., and also from coal when distilled at a comparatively low temperature. Most descriptions of natural petroleum consist of a mixture of all the members of this series. In coal-tar they play a subordinate part; but if, in gas-making, coal has been partly replaced by browncoal, shale, cannel-coal, etc., the tar is much richer in aliphatic hydrocarbons, and may easily contain so much of them that the extraction of the aromatic hydrocarbons does not pay—especially as the aliphatic hydrocarbons are most objectionable impurities in commercial benzol, which, if they occur to any great extent, may render it unfit for the manufacture of nitrobenzol.

The compounds of this class are distinguished from the non-saturated hydrocarbons (the ethylene and acetylene series) by not being absorbed by sulphuric acid or bromine; this behaviour can be utilized for separating the two classes. From benzene and its homologues they are distinguished through being hardly at all acted upon by nitric acid in the cold, and not forming nitro-compounds.

The lowest members, up to butane, are at the ordinary temperature gaseous, but may occur in tar in a state of solution, all the more readily as they are easily soluble in ether and alcohol, and thus probably also in benzene, etc. The members from pentane upwards are liquid; up to decane they have been observed in tar. The highest members, beginning from  $C_{28}H_{58}$ , are solid, and form paraffin proper: whether this occurs in tar obtained exclusively from ordinary coal is doubtful.

#### *Methane, CH<sub>4</sub>.*

*Synonyms*—methylic hydride, marsh-gas, fire-damp, light carburetted hydrogen. A colourless gas, devoid of smell or taste; sp. gr. 0.5566 (air=1). At 0° C. 100 vols. of water absorb 5.45 vols.; alcohol, nearly half its volume. It burns with a pale yellow flame. Passed through red-hot tubes it yields acetylene, benzene, naphthalene. Mixed with air it gives a very explosive mixture.

*Ethane*,  $C_2H_6$ .

*Syn.* dimethyl, ethylic hydride. A gas without colour or smell; sp. gr. 1.075; condenses at  $4^\circ$  to a liquid under a pressure of 46 atmospheres. Water dissolves at  $0^\circ$  9.45 per cent. by volume; alcohol,  $1\frac{1}{2}$  times its volume. Burns with a bluish, non-luminous flame.

*Propane*,  $C_3H_8$ .

*Syn.* propylic hydride. A gas, condensing to a liquid below  $-20^\circ C.$ ; alcohol dissolves six times its volume.

*Butane*,  $C_4H_{10}$ .

*Syn.* diethyl, butylic hydride. Two isomers are possible and known; only normal butane, however,  $CH_3-CH_2-CH_2-CH_3$ , has been found in mineral oils. A gas of sp. gr. 2.01 (air=1). Authorities differ widely as to its liquefying-point. Frankland puts it at  $-23^\circ$ ; Butlerow at  $+1^\circ$ , and, under pressure of  $2\frac{1}{4}$  atmospheres, at  $+18^\circ$ . In water it is next to insoluble. Alcohol at  $14^\circ C.$  and 745 mm. pressure dissolves 18.13 vols. It burns with a strongly luminous flame.

*Pentane*,  $C_5H_{12}$ .

*Syn.* amyllic hydride. Of the three isomers the normal and isopentane,  $CH_3-CH_2-CH(CH_3)_2$ , have been found in cannell- and boghead-tar. Schorlemmer found in coal-tar only normal pentane.

Normal pentane boils at from  $37^\circ$  to  $39^\circ C.$ ; sp. gr. at  $18^\circ = 0.6263$  (water=1). Isopentane boils at  $30^\circ$ ; sp. gr. at  $18^\circ = 0.628$ . Both are colourless, very mobile liquids, somewhat similar to chloroform, miscible with ether and alcohol in every proportion, solvents for fats; they burn with a brilliant white flame.

*Hexane*,  $C_6H_{14}$ .

*Syn.* caproylie hydride. Five isomers; the normal one occurs in petroleum, boghead- and cannell-tar; it is the principal constituent of the most volatile petroleum-ether (gasoline). Boils at  $69^\circ$  to  $71^\circ$ ; sp. gr. at  $17^\circ = 0.663$ . Colourless.



mobile liquid, of faintly ethereal smell, insoluble in water, miscible with ether, alcohol, acetone, etc. (this solubility holds good for all the higher members as well). Burns with a bright, luminous flame.

Warren found another hexane in petroleum, boiling at  $61^{\circ}\cdot3$ , which Schorlemmer could not discover in that substance.

*Heptane, C<sub>7</sub>H<sub>16</sub>*

*Syn.* œnanthylic hydride. Nine isomers possible. The different tars contain the normal one, boiling at  $98^{\circ}$ ; sp. gr. at  $0^{\circ}=0\cdot7006$ , at  $15^{\circ}=0\cdot6886$ ; also ethylisoamyl, boiling at  $90^{\circ}\cdot3$ ; sp. gr. at  $0^{\circ}=0\cdot6969$ . Mobile liquids, of faint, pleasant smell; burn with a somewhat smoky flame.

*Octane, C<sub>8</sub>H<sub>18</sub>*

*Syn.* caprylic hydride, dibutyl, valyl. Of the eighteen possible isomers, one boiling at  $119^{\circ}$  or  $120^{\circ}$  (sp. gr. at  $17^{\circ}=0\cdot719$ ), and another, probably the normal one, boiling at  $124^{\circ}$  (sp. gr. at  $0^{\circ}=0\cdot7188$ ), have been found in petroleum, boghead- and coal-tar. Ahrens<sup>1</sup> found an octane in the oils distilling after the nitration of toluene, boiling at  $121^{\circ}$  to  $122^{\circ}$ , sp. gr.  $0\cdot7245$  at  $23^{\circ}$  C. They are limpid liquids with an ethereal smell and somewhat burning taste. The ordinary petroleum-spirit ligroine of commerce contains principally heptane and octane.

*Nonane, C<sub>9</sub>H<sub>20</sub>*

That found in petroleum boils, according to Wurtz, at  $130^{\circ}$  to  $132^{\circ}$  (sp. gr. at  $6^{\circ}=0\cdot7242$ , smell like oranges); according to Beilstein, at  $150^{\circ}\cdot8$ . Which is right? Refined petroleum (kerosene) contains from C<sub>9</sub>H<sub>20</sub> up to C<sub>16</sub>H<sub>34</sub>, along with hydrocarbons of the formula C<sub>n</sub>H<sub>2n</sub>.

*Decane, C<sub>10</sub>H<sub>22</sub>*

*Syn.* diamyl. Found in all tars, probably the isomer diisoamyl. Boils at  $158^{\circ}$  to  $159^{\circ}$ ; at  $-30^{\circ}$  it gets viscid; sp. gr. at  $18^{\circ}=0\cdot736$ . Beilstein states that the boiling-point is  $161^{\circ}$ , the sp. gr. at  $16^{\circ}=757$ . O. Jacobsen<sup>2</sup> has found a

<sup>1</sup> *Ber.*, 1907, p. 848.

<sup>2</sup> *Ann. Chem.*, clxxxiv., p. 179.

decane, boiling at  $170^{\circ}$  to  $171^{\circ}$ , in the fractions of light coal-tar oil which pass over between  $163^{\circ}$  and  $168^{\circ}$ , along with pseudocumene and mesitylene. Schultz and Hartog<sup>1</sup> have proved with certainty the presence of normal decane in coal-tar.

*Undecane,  $C_{11}H_{24}$ .*

Found in American petroleum. Boils at  $180^{\circ}$  to  $182^{\circ}$ ; sp. gr. at  $16^{\circ} = 0.765$ .

*Duodecane,  $C_{12}H_{26}$ .*

*Syn.* dicaproyl, dihexyl, laurylic hydride. Found in bog-head-tar and petroleum. An oily, colourless liquid, with a pleasant, turpentine-like smell, boiling at  $200^{\circ}$  to  $202^{\circ}$ ; sp. gr. at  $18^{\circ} = 0.7568$ ; burns with a luminous flame without much smoke.

*Higher members.*

$C_{13}H_{28}$	boiling-point	$218-220^{\circ}$ ,	spec. grav.	0.778
$C_{14}H_{30}$	"	$236-240^{\circ}$ ,	"	0.796
$C_{15}H_{32}$	"	$258-262^{\circ}$ ,	"	0.809
$C_{16}H_{34}$	"	about $280^{\circ}$ .		

*Solid Paraffin*

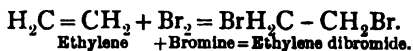
contains bodies of the formula  $C_{17}H_{36}$  up to  $C_{27}H_{56}$ ; also usually about 1 per cent. of oxygen. The paraffin found in the highest-boiling portions of real coal-tar is, according to Perkin, unlike ordinary paraffin; it fuses at a higher temperature, and is but slightly soluble in petroleum or naphtha. The proper paraffins occur principally in tar from Scotch and Lancashire cannel-coal.

HYDROCARBONS OF THE ETHYLENE SERIES  $C_nH_{2n}$  (OLEFINS).

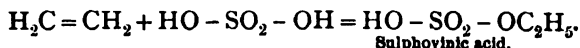
The lowest members of this series are gaseous at the ordinary temperature, but occur constantly in illuminating gas, and probably dissolved in tar. The higher members are liquid; the highest solid. It is characteristic of all to unite directly with chlorine, bromine, or iodine, forming oily liquids; with bromine especially the reaction is very violent. This is ascribed to the circumstance that they are non-saturated

<sup>1</sup> *Berl. Ber.*, 1909, p. 3609.

compounds ("dyad radicals"), in which carbon occurs doubly tied, so that, when one of these ties is broken, two monovalent atoms can attach themselves directly; *e.g.*,



They also unite readily with the halogen hydrides HCl, HBr, and especially HI; also with hypochlorous acid, forming chlorhydrines, *e.g.*,  $\text{CH}_2(\text{OH})-\text{CH}_2\text{Cl}$ . Concentrated sulphuric acids absorb them, the lower members only at higher temperatures, also by direct attachment and formation of sulphonic acids; *e.g.*,



From this it follows that these compounds can be removed from the tar-oils by bromine or by concentrated sulphuric acid. In ordinary coal-tar they play but an insignificant part; but they occur copiously in cannell- and boghead-tar. They may possibly have been confounded with the addition-products of benzene, observed only recently (naphthenes, etc.).

#### *Ethylene, C<sub>2</sub>H<sub>4</sub>.*

*Syn. elayl.* Liquefies at 0° only under a pressure of 42½ atmospheres, at -110° under the ordinary pressure. Sp. gr. 0.9784. Water at 9° dissolves 0.25 vol.; at 15°, 0.16 vol. Much more dissolves in alcohol, ether, oil of turpentine, petroleum (about 2½ vols.), hence probably also in tar-oils. Concentrated sulphuric acid absorbs it on prolonged agitation, better at 160° to 175° C.; fuming oil of vitriol much more quickly, with formation of ethionic acid. Armstrong and Miller<sup>1</sup> have found it in the "hydrocarbon" condensed from Pintsch gas, as well as propylene, normal amylene, normal hexylene, and normal heptylene.

#### *Propylene, C<sub>3</sub>H<sub>6</sub>.*

*Syn. tritylene.* Not yet liquid at -140°, possessing a garlic-like smell. One hundred vols. of water dissolve at 0° 44 vols., at 15° 23 vols.; absolute alcohol 12 to 15 vols., glacial acetic acid 5 vols. Its chemical behaviour is similar to that of ethylene.

<sup>1</sup> *J. Chem. Soc.*, xlix, p. 74.

*Butylene, C<sub>4</sub>H<sub>8</sub>.*

*Syn.* tetrylene, ditetryl. Three isomers are possible and known. First condensed by Faraday from the illuminating-gas obtained from fatty oils, by strong pressure. Normal butylene,  $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$ , boils at  $-5^\circ$ ; pseudobutylene,  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$ , at  $+1^\circ$ ; isobutylene,  $(\text{CH}_3)_2\text{C}=\text{CH}_2$ , at  $-7^\circ$  or  $-8^\circ$ .

Normal butylene has been obtained from the light oils of the compressed gas from boghead-coal by Brochet (*Comptes rend.*, cxiv., p. 601). In the first runnings of coal-tar it has been found by Ahrens (*Z. angew. Chem.*, 1904, p. 1518).

*Amylene, C<sub>5</sub>H<sub>10</sub>.*

*Syn.* pentylene, valerene. Of the five possible isomers, only that is well known which is obtained from amylic alcohol by water-abstracting reagents, especially zinc chloride. Whether this is identical with the amylene found in coal-tar,<sup>1</sup> and much more abundantly in boghead-tar, petroleum, etc., or not, is not quite certain; but it is usually assumed to be the same. At all events several amylenes occur in tar, probably also polymers (*cf.* Brochet, *Comptes rend.*, cxiv., p. 601).

Ordinary amylene is a limpid, mobile liquid, of cooling, astringent, and somewhat pungent taste, and smelling somewhat like rotten cabbages. Its boiling-point is variously stated at from  $33^\circ$  to  $42^\circ$  (that obtained from amylic alcohol boils at  $39^\circ$ ). Sp. gr. at  $10^\circ = 0.6549$ . Is is but sparingly soluble in water, but indefinitely miscible with alcohol. Like its congeners it unites directly with Cl, Br, HCl, HBr, HI, also with  $\text{NO}_2$  and  $\text{HOCl}$ . Oxidising substances (potassium permanganate, chromic acid, etc.) convert it into aliphatic acids, carbon dioxide, ketones, etc. With sulphuric acid, Berthelot states,<sup>2</sup> it yields an acid isomer to sulphamylic acid, which Erlenmeyer<sup>3</sup> could not find. However this may be, all the isomers dissolve in sulphuric acid at ordinary temperatures, some of them even when this is not fully concentrated.

<sup>1</sup> Helbing, *Annalen*, clxxii., p. 281. Ahrens, *Z. angew. Chem.*, 1904, p. 1518. Watson Smith (priv. comm.) has also found amylene in the first runnings of London tar, together with carbon bisulphide.

<sup>2</sup> *Comptes rend.*, lvi., p. 1242.

<sup>3</sup> *Z. für Chemie*, 1865, p. 362.

Amylene was used for some time as an anæsthetic, in lieu of chloroform.

*Hexylene, C<sub>6</sub>H<sub>12</sub>*

*Syn.* caproylene. Of the many isomers, tar seems to contain essentially the normal, the only one pretty well known; but other isomers are probably present as well (*cf.* Brochet, *loc. cit.*). Normal hexylene is a colourless, mobile liquid, smelling like amylene, boiling at 68° to 70°; sp. gr. at 0° = 0.6996; insoluble in water, readily soluble in ether and alcohol; chemically quite analogous to amylene. Sulphuric acid, diluted with  $\frac{1}{3}$  vol. water, dissolves in the cold its volume of hexylene, from which mixture secondary hexylic alcohol soon separates. Concentrated sulphuric acid colours it reddish brown, gives off SO<sub>2</sub>, and turns it into a thick oil.

*Heptylene, C<sub>7</sub>H<sub>14</sub>*

*Syn.* œnanthylene. Like the above, found in boghead-tar. A limpid, mobile liquid with a garlic-like smell. Boils at 94° (Pelouze and Cahours), 96° (Schorlemmer), 99° (C. G. Williams). Sp. gr. at 18° = 0.718 (C. G. Williams), at 17.5° = 0.7388 (Schorlemmer). Its chemical behaviour is like that of the two last-mentioned compounds.

AROMATIC ADDITION-PRODUCTS, C<sub>n</sub>H<sub>2n</sub> (NAPHTHENES).

According to Beilstein and Kurbatow,<sup>1</sup> the hydrocarbons of Caucasian petroleum having the formula C<sub>n</sub>H<sub>2n</sub> are not identical with the compounds of the preceding series; such occur also in American petroleum along with heptane, etc. They were found identical with the hydrogen addition-products of aromatic hydrocarbons discovered by Wreden,<sup>2</sup> viz. :—

	Sp. gr. at 0°.	Boils at
Hexahydrobenzene . C <sub>6</sub> H <sub>12</sub>	0.76	69° C.
Hexahydrotoluene . C <sub>7</sub> H <sub>14</sub>	0.772	97° „
Hexahydroisoxylene . C <sub>8</sub> H <sub>16</sub>	0.777	118° „

Schützenberger and Ionine,<sup>3</sup> who confirmed the above, proposed the name *paraffenes* for these compounds, which

<sup>1</sup> *Ber.*, 1880, pp. 1818, 2028.

<sup>2</sup> *Liebig's Annalen*, clxxxvii., p. 166.

<sup>3</sup> *Comptes rend.*, xci., p. 828.

are inactive towards bromine, sulphuric acid, and nitric acid. Armstrong and Miller<sup>1</sup> found these saturated hydrocarbons of the formula  $C_nH_{2n}$ , which they call "pseudolefines," in the "hydrocarbon" condensing from Pintsch gas.

Markownikoff, (*Ann. Chem. Pharm.*, ccxxxiv., p. 89), without denying the existence of hexahydrobenzene, etc., declared that most of what had been taken for these compounds belongs to a new class of compounds, which he calls "naphthenes." Later on (*Berl. Ber.*, xx., p. 1850) he practically confirmed the views of Beilstein and Kurbatoff. Kraemer and Böttcher (*Berl. Ber.*, 1887, p. 595) confirmed and amplified the previously made observations on the occurrence of addition-products of the benzene series which they take to be identical with Markownikoff's "naphthenes." They retain that designation for these compounds which are distinguished from the olefines isomeric with them, particularly by not combining with bromine and not being soluble in concentrated sulphuric acid. In the coal-tar oils they occur together with real paraffins. Engler and his co-operators (*Dingl. polyt. J.*, cclxxi., p. 515; Inaug. Diss. of Dengler [1888] and Schneider [1893]) have found naphthenes in nearly all descriptions of petroleum, also in the products artificially obtained by distilling aliphatic matters under high pressure. Renard (*Ann. Chim. Phys.* [6], i., p. 223) found them in essence of rosin, Heusler (*Berl. Ber.*, 1895, p. 488) in oils from lignite-tar.

Ahrens and Modzdenski (*Z. angew. Chem.*, 1908, p. 1411) found the nononaphthene,  $C_9H_{18}$ , of sp. gr. 0.7862, boiling at  $137^\circ$  to  $139^\circ$ , in the waste oil from the preparation of nitroxylene, which proves the presence of naphthenes in coal-tar.

Maquenne (*Comptes rend.*, cxiv., pp. 918 and 1066; *Ann. Chim. Phys.* [6], xxviii., p. 270; *Berl. Ber.*, 1895, p. 488) made an interesting observation, concerning the formation of naphthenes. He found that the terpene occurring in essence of rosin,  $C_7H_{12}$ , which must undoubtedly be considered as tetrahydrotoluene, under the influence of concentrated sulphuric acid is converted into hexahydrotoluene. He consequently considers it doubtful whether the essence of rosin contains any naphthenes preformed; much of these, perhaps the whole, has been evidently formed in the sulphuric acid treatment from heptane,

<sup>1</sup> *J. Chem. Soc.*, xlix., p. 90.

a phenomenon which, he thinks, may also take place with coal-tar and lignite oils. But for lignite oils, Heusler (*vide supra*) has proved since then the original presence of naphthenes.

The views of Beilstein and Kurbatoff on the constitution of the naphthenes were later on completely confirmed by Markownikoff and Spady (*Berl. Ber.*, xx., p. 1850), who found that carefully purified octonaphthene, on being treated with sulphur, gives off hydrogen sulphide, and that the product of the reaction, on being nitrated, yields large quantities of trinitro-*m*-xylene. This proves that the octonaphthene had been converted by the treatment with sulphur into metaxylene, which is only possible on the assumption that it must be considered as hexahydroxylene.

Synthetically, apart from the hexamethylene boiling at 79° to 79.5°, prepared by Baeyer (*Ann. Chem. Pharm.*, cclxxviii., p. 111), whose behaviour was too little known to allow of making a certain inference on the constitution of naphthenes, no other member of that series had been obtained, and therefore no certain proof for the hydro-aromatic nature of these hydrocarbons had been adduced. But Zelinski (*Berl. Ber.*, 1895, p. 780) and Reformatzki (*ibid.*, 1896, p. 214) have filled up this gap by the synthetic production of an octonaphthene and a nononaphthene.

The originally aromatic nature of the naphthenes is also proved by the following observations. Spindler (*Berl. Ber.*, 1891, Ref. p. 563) obtained from heptanaphthene, produced from Caucasian crude naphtha, by treatment with bromine in presence of aluminium chloride quite smoothly pentabrominated toluene, according to which result naphthene must be a hexahydrotoluene. Konowaloff (*ibid.*, 1890, p. 431) found that a nononaphthene, coming from the same source, dissolved completely in fuming oil of vitriol, with formation of pseudo-cumene-sulphonic acid.

Further researches in that domain have been made by Konowaloff and Markonikoff (*J. prakt. Chem.*, xlv., p. 561; xlv., p. 86; *Berl. Ber.*, xviii., Ref. 23, 186, 431), Zaloziecki (*Dingl. polyt. J.*, ccxc., p. 115); Maquenne (*loc. cit.*); Bruhn (*Chem. Zeit.*, 1898, p. 908), Wischin (*Die Naphthene des Erdöls und ihre Stellung zu anderen hydrierten Kohlenwasserstoffen*,

*Braunschweig*, 1901). We may take it as proved that the terpenes, naphthylenes, and naphthenes are all hydrides of aromatic hydrocarbons, the empirical composition of which can be expressed by the following formulæ :—

$C_nH_{2n-6}$	.	.	.	.	Benzenes
$C_nH_{2n-6}+H_2$	.	.	.	.	Terpenes
$C_nH_{2n-6}+H_4$	.	.	.	.	Naphthylenes
$C_nH_{2n-6}+H_6$	.	.	.	.	Naphthenes

The naphthenes, therefore, represent the highest degree of hydration of the aromatic hydrocarbons.

The naphthenes are colourless liquids, smelling slightly like petroleum, hardly changing on standing in contact with air, completely oxidised by the ordinary oxidising agents. They are substituted by bromine only at higher temperatures, similar to the paraffins, from which they differ by the higher specific gravity of the compounds containing the same number of carbon atoms.

Engler and Schneider have based upon this a method for distinguishing naphthenes and paraffins by their respective refractive indices (Schneider's Inaug. Diss., Karlsruhe, 1888). If we compare the specific gravities of the paraffins, olefines, aromatic hydrocarbons, and naphthenes containing the same number of carbon atoms, we find that the paraffins have the lowest, and the aromatic hydrocarbons the highest specific gravities, while the naphthenes and olefins range between them. The same ratio holds good as to the refractive indices. If we call the refractive index  $E$ , and the specific gravity at the same temperature  $S$ , the specific refractive index is  $\frac{E-1}{S}$ . This is again highest for the benzenes, followed by the indices for olefins, paraffins, and hexahydrides, as shown by the following table :—

	Specific gravity.	Refractive Index.	Specific Refraction.
Hexane . . .	0.6630 (17°)	1.3717	0.5605
Hexylene . . .	0.6997 (0°)	1.3989	0.5702
Benzene . . .	0.8799 (20°)	1.5043	0.5731
Hexahydrobenzene .	0.7600 (0°)	1.4126	0.5429



If, therefore, we remove from a mixture of all these bodies the benzenes by means of sulphuric acid, all the three factors must be smaller in the residue. If we now remove the naphthenes by fuming oil of vitriol, so that only the paraffins remain behind, the specific gravity and refractive index of the residue will be again smaller, but the specific refraction will be greater.

Pictet and Bouvier (*Comptes rend.*, 1913, pp. 779 and 1436; *Ber.*, 1913, p. 3342; *Chem. Zeit.*, 1914, p. 1025; *J. Soc. Chem. Ind.*, 1913, p. 1098; 1914, p. 70; 1915, p. 163), by distilling coal in a vacuum at a temperature of only  $450^{\circ}$ , have obtained a "vacuum tar" containing a number of hitherto unknown hydro-aromatic hydrocarbons which may [or may not!] occur in ordinary coal-tar as well, but it would be anyhow too difficult and without any technical interest, to isolate them from that.

#### HYDROCARBONS OF THE ACETYLENE SERIES, $C_nH_{2n-2}$

*Acetylene* itself,  $C_2H_2$ , is a gas, and can be dissolved only in very small quantity in tar. Schorlemmer (*Chem. News*, xiii., p. 253) found in the light oil from cannel-coal, after treatment with sulphuric acid, polymers of the acetylene series having the general formula  $(C_nH_{2n-2})_2$ , viz. :—

$C_{12}H_{20}$	boiling at $210^{\circ}C$ .
$C_{14}H_{24}$	„ $240^{\circ}$ „
$C_{16}H_{28}$	„ $280^{\circ}$ „

They are colourless, oily liquids, lighter than water, smelling like carrots or parsnips. They unite directly with bromine, with a violent reaction; in concentrated nitric acid they dissolve; and on diluting the solution with water, only nitro-compounds separate. Since the original oils boiled below  $120^{\circ}$ , they cannot have contained these bodies, but those of the acetylene series,  $C_nH_{2n-2}$ , itself. In coal-tar they probably play even a less important part than in cannel-tar. But to acetylene itself a very important function in the formation of aromatic hydrocarbons is ascribed (see below, p. 226).

Acetylene is now technically prepared in large quantities by

decomposing calcium carbide with water, and furnishes an excellent gaseous illuminant.

*Allylene*,  $C_3H_4$ .

*Normal allylene*,  $CH_3-C\equiv CH$ , discovered in 1861 by Sawitsch and by Markownikoff. Colourless gas, smelling like acetylene, soluble in water and especially in alcohol.

*Isoallylene*,  $CH_2=C=CH_2$ , discovered in 1872 by Aarland.

The allylenes have not yet been proved to exist in coal-tar; but they most probably do occur there, and play an important function like that of acetylene.

*Crotonylene*,  $C_4H_6$ .

Discovered in 1863 by Caventou<sup>1</sup>; since then prepared synthetically and found in coal-tar<sup>2</sup> and in Pintsch tar.<sup>3</sup> Possibly the latter is isomeric with the crotonylene from coal-tar, and is not a true acetylene,  $C_2H_5.C\equiv CH$ , or else dimethylene-ethane,  $CH_2=CH-CH=CH_2$ , or else dimethyl-acetylene,  $CH_3.C\equiv C.CH_3$ .

Crotonylene is a colourless liquid, boiling at  $18^\circ$ .

Isomeric with crotonylene is the 1 : 3 *butadiene* (vinylethylene, erythrene, pyrrolyten), whose presence in coal-tar had been made probable by Kraemer and Spilker's discovery of cyclopentadiene (*Berl. Ber.*, xxix., p. 552), and which had been separated by Caventou (*ibid.*, vi., p. 70) from compressed illuminating gas, and also obtained by passing fusel-oil vapours through red-hot tubes. Contrary to the hydrocarbons of the acetylene series, it does not produce any precipitate in ammoniacal cuprous-chloride solution. According to a private communication to Dr Koehler, Spilker and Weissgerber have obtained it recently from "first runnings" of benzol, where it is present in a quantity of 2 to 5 per cent. of the total benzol. This discovery is of considerable importance in view of the recently published processes for manufacturing *synthetic india-rubber* from methyl-butadiene and other derivatives of butadiene. Patents have been applied for by the Gesellschaft für

<sup>1</sup> Caventou, *Bull. Soc. Chim.* [2], xix., p. 245.

<sup>2</sup> Helbing, *Annalen*, clxxii., p. 281.

<sup>3</sup> Armstrong and Miller, *J. Chem. Soc.*, xlix., p. 80.

Teerverwertung in Duisburg-Meiderich, for the recovery of crude butadiene and its conversion into an indiarubber-like substance. Such crude mixtures can be obtained from the crude benzol, both that distilled from gas-works tar and from coke-oven tar, by fractionating the "first runnings"; also from the product made by compression or cooling. These mixtures, on being treated by metallic sodium, are to a great extent converted into a substance resembling indiarubber. According to the patent application, first runnings from crude benzol, previously freed from carbon disulphide by well-known means, are cooled down to at least  $-10^{\circ}$ , and fractionally distilled until the vapours passing over show a temperature of  $25^{\circ}$ ; 100 parts of the distillate are mixed with 2 parts sodium (in the shape of wire or ribbon) and allowed to stand at the ordinary temperature. After a short time the sodium compounds of the acetylene hydrocarbons separate out in the form of a white or light yellow powder, which sinks to the bottom; thereupon the polymerization of the remaining hydrocarbon sets in and the contents of the vessel is converted into a jelly-like mass. When no more thickening takes place, the whole is diluted with benzol, the sodium compounds are removed by decanting or filtering, and the indiarubber is precipitated from the solution by alcohol. The presence of small quantities of ammonia promotes the polymerization. If the total annual production of benzol in Germany is put = 100,000 tons, it would be possible to obtain from it 2000 to 5000 tons of butadiene, and the same quantity of artificial indiarubber, which would be about 2.5 to 6.5 per cent. of the present annual production of india-rubber = about 80,000 tons.

*Valylene*,  $C_6H_8$

*Syn.* piperylene. Roscoe,<sup>1</sup> in "first runnings" from coal-tar, discovered a compound, spontaneously formed by polymerization of the fraction boiling at  $30^{\circ}$ , and exhibiting the composition  $C_{10}H_{12}$ , melting at  $32^{\circ}.9$ . He considers it possible that this may have been formed from *valylene*,  $C_6H_8$ , but a search for that body proved unsuccessful. Etard and Lambert,<sup>2</sup> as well

<sup>1</sup> *J. Chem. Soc.*, xlvii., p. 669.

<sup>2</sup> *Comptes rend.*, 1891, cxii., p. 945.

as Kraemer and Spilker,<sup>1</sup> proved that hydrocarbon not to be valylene, but pyropentylene or cyclopentadiene. Brochet, however,<sup>2</sup> isolated true valylene or "piperylene" from the compressed oil from boghead or schist, boiling at 41° or 42°.

*Hexoylene, C<sub>6</sub>H<sub>10</sub>*

*Syn.* diallyl. A colourless liquid, with a penetrating alliaceous smell, boiling at 76° to 80°; sp gr. at 13° = 0.71.

HYDROCARBONS OF THE SERIES C<sub>n</sub>H<sub>2n-4</sub>.

One such, *nonone*, C<sub>9</sub>H<sub>14</sub>, the next lower homologue of oil of turpentine, has been found by Tawildarow<sup>3</sup> in tar, viz. in the portion distilling after cumene, between 175° and 190°. On fractionating, most came over at 174°. This body does not appear to have been obtained in a pure state, and its existence cannot be considered completely established. It is possibly identical with Baeyer's synthetically prepared *dihydro-cymene* (*Berl. Ber.*, 1893, p. 232).

*Cyclopentadiene, C<sub>5</sub>H<sub>6</sub>*

*Syn.* pyropentylene. Obtained in an impure state by Roscoe, in a pure state by Etard and Lambert (*Comptes rend.*, cxii., p. 945), from the condensation-products of oil-gas. Boils at 42°·5; sp. gr. 1.803. Kraemer and Spilker (*Berl. Ber.*, 1896, p. 552) obtained it also from the first runnings of coal-tar benzol; they state the boiling-point = 41°; sp. gr. at 15° = 0.815.

It has a peculiar smell; it is insoluble in water, but miscible in all proportions with alcohol, ether, and benzene. Concentrated sulphuric acid carbonizes it with explosive violence; dilute acid causes it to "resinify." Chlorine, bromine, and iodine easily form addition-products; also aqueous sulphurous acid, the latter forming a compound C<sub>10</sub>H<sub>12</sub>·2H<sub>2</sub>SO<sub>3</sub>, soluble in alkali, but insoluble in nearly all other reagents. Silver nitrate is at once reduced by it.

Cyclopentadiene polymerizes even in the cold quite spontaneously to a solid, *dicyclopentadiene* (C<sub>5</sub>H<sub>6</sub>)<sub>2</sub>, which exhibits

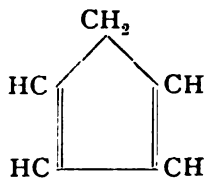
<sup>1</sup> *Berl. Ber.*, 1896, p. 1152.

<sup>2</sup> *Comptes rend.*, cxiv., p. 601.

<sup>3</sup> *Z. für Chemie*, [2], 1868, iv., p. 278.

all the essential properties of oil of turpentine; boiling-point,  $170^{\circ}$ ; melting-point,  $32.5^{\circ}$ ; sp. gr. 0.9766.

Extensive investigations on cyclopentadiene have been made by I. Thiele.<sup>1</sup> The structural formula of cyclopentadiene is:

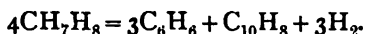


*Nonene*,  $\text{C}_9\text{H}_{14}$ .

Boiling-point,  $174^{\circ}$  C. Found by Tawildaroff in coal-tar. Possibly identical with Baeyer's synthetically produced *Dihydrocymene* (*Berl. Ber.*, 1893, p. 232).

#### HYDROCARBONS OF THE BENZENE SERIES, $\text{C}_n\text{H}_{2n-6}$ .

The compounds of this series, which belong to the large class of the so-called aromatic compounds, are specifically characteristic of coal-tar. They occur also in the tar from wood, brown coal, shale, etc., but therein occupy a subordinate position.<sup>2</sup> But they are also formed by many reactions; above all by the action of heat, partly from their own higher homologues or other derivatives, partly by the decomposition or by the molecular condensation of aliphatic compounds. By the action of high temperatures, *e.g.*, by passing the vapours through red-hot tubes, benzene is formed not merely from toluene, xylene, styrolene, etc., but also from alcohol, acetic acid, ethylene, methane, frequently together with naphthalene; *e.g.*—



<sup>1</sup> *Berl. Ber.*, 1909, p. 666.

<sup>2</sup> Markownikoff (*Ann. Chem. Pharm.*, ccxxiv., p. 89) has found in Caucasian petroleum large quantities of benzene, toluene, xylenes, pseudocumene, mesitylene, durene, isodurene, diethyltoluene, and other hydrocarbons of the formulæ  $\text{C}_{11}\text{H}_{14}$ ,  $\text{C}_{11}\text{H}_{12}$ ,  $\text{C}_{12}\text{H}_{14}$ ,  $\text{C}_{13}\text{H}_{14}$ . If these discoveries, which are certainly in opposition to the assertions of all previous investigators, were confirmed, it would become doubtful how much of the aromatic hydrocarbons, found after passing petroleum residues through red-hot tubes, are newly formed, and how much was already pre-existent in the original substance.

Of course, even more highly condensed molecules, such as anthracene, phenanthrene, chrysene, etc., are formed in a similar way, hydrogen being eliminated. By passing the mixed vapours of benzene and toluene through red-hot tubes, Carnelly<sup>1</sup> obtained naphthalene, diphenyl, paratolylphenyl, orthoparadi-phenyl, two methylene-diphenylenes, phenanthrene, anthracene, paradiphenyl-benzene, a hydrocarbon  $C_{32}H_{28}$ , a liquid hydrocarbon fusing at  $13^\circ$  and boiling at  $290^\circ$  to  $316^\circ$ , two other liquid hydrocarbons (or mixtures of hydrocarbons) boiling at  $359^\circ$  to  $383^\circ$  and  $404^\circ$  to  $427^\circ$ , and solid black bitumen.

Ferko (*Berl. Ber.*, 1887, p. 105) passed the vapours of benzene, toluene, and naphthalene, together with ethylene, through a red-hot iron tube. He obtained from benzene + ethylene: carbon, hydrogen, diphenyl, styrol, anthracene, and phenanthrene. Toluene, whether mixed with ethylene or not, by that treatment yielded benzene, naphthalene, styrol, anthracene, and a little phenanthrene. Naphthalene yielded diphenyl; naphthalene + ethylene yielded dinaphthyl, a little phenanthrene, and acenaphthene. Ethylbenzol yielded benzene, toluene, styrol, naphthalene, diphenyl, phenanthrene, and anthracene.

Norton and Noyes (*Amer. Chem. J.*, viii, p. 362), on passing pure acetylene gas through a red-hot pipe, obtained benzene, naphthalene, anthracene, methane, ethane, propylene, butylene, and crotonylene.

It thus becomes conceivable why destructive distillation at lower temperatures yields more of fatty bodies and less of permanent gases, at higher temperatures more of aromatic compounds and more of permanent gases, and why, by passing the heavy hydrocarbons of the aliphatic class (from wood-tar, shale-tar, petroleum, etc.) through red-hot tubes, benzene and its derivatives can be prepared on a large scale (pp. 185 *et seq.*).

We shall return to this subject when treating of the theory of the formation of tar.

### *Benzene, $C_6H_6$ .*

*Syn.* benzol (this word is now mostly used for the commercial mixture of benzene, toluene, etc., in varying quantity), phenylic hydride. It is usually stated that benzene was discovered in

<sup>1</sup> *J. Chem. Soc.*, 1880, p. 701.

1825, by Faraday, in the liquid separating from condensed oil-gas, but Schelenz (*Z. angew. Chem.*, 1908, p. 2577) has shown that the compound which we now term "benzol," or more recently "benzene," had been discovered in coal-tar forty years before Faraday in the year 1825 reported "On new compounds of carbon and hydrogen, and on certain other products obtained during the decomposition of oil by heat." In Macquer-Leonhardi's *Chymisches Wörterbuch*, published at Leipzig in 1783, vol. i., pp. 86, 709, a passage is found which in English translation runs as follows:—"From coal we can obtain by distillation a nearly tasteless water, a brownish-yellow, disagreeably balsamically smelling oil, and another empyreumatic, tougher oil which can be rectified into naphthol (that is, 'mountain-oil,' in the old classic sense), like petroleum." In 1784 was published at Leipzig, *Demady's Laborant*, translated into German by Samuel Hahnemann, in which the distillation of coal on the large scale is described, enumerating the various fractions, one of which can be at once put into bottles in which a space of at least 3 or 4 fingers' breadth must be left. Even before this, in Caspar Neumann's *Praelectiones Chemicæ*, published at Schneeberg in 1740, it is stated that "fossile carbons" on distillation yield a little water and "a sharply tasting spirit," which must have been benzol.

Mitscherlich called the substance which he obtained in 1833 by the distillation of benzoic acid with lime, "benzin." It is not quite certain whether the designation "benzol" was first used by Faraday or by Liebig; "benzène" appears in French publications of 1861. In the same year Hirzel recommended "benzol from coal-tar," mixed with magnesia, as a detergent. Confusions with "benzin" from petroleum were still very frequent, until for Germany the official *Deutsches Arzneibuch* in 1882 made a definite distinction between "benzinum petrolei" and "benzol from coal-tar." This is practically the same distinction as is made in England.

The term "benzene" is everywhere understood to mean the pure compound  $C_6H_6$ , for which, however, the designation "benzol" is also frequently employed, *e.g.* in the pharmacopœia. The term "benzin" is reserved for the quite different hydrocarbons distilled from petroleum. Mitscherlich, in 1833, prepared it by the dry distillation of calcium benzoate, determined its empirical

formula, and conferred upon it its present name; he also discovered nitrobenzene. The first discovery of benzene in *coal-tar* is claimed by Leigh, who states that his communication to that effect made to the British Association meeting in 1842 was by an oversight omitted in its Report.<sup>1</sup> At all events his observation remained unknown and sterile; and the credit of having, in 1845, distinctly recognized the presence of benzene in coal-tar, and proved it by transforming it into nitrobenzene and aniline, will not be denied to A. W. Hofmann.<sup>2</sup> The process for obtaining it in any quantity from coal-tar was worked out in his laboratory by one of his pupils, Charles Mansfield,<sup>3</sup> who carried out the process on the large scale and minutely described the principle of dephlegmation for separating the various hydrocarbons; he distinctly pointed out that the apparatus employed in rectifying spirit might be employed for this purpose, even with greater advantage than for spirit of wine itself<sup>4</sup>—a suggestion usually, but erroneously, ascribed to E. Kopp, who first mentions it in 1860.<sup>5</sup> Mansfield fell a victim to his discovery. On the 17th of February 1854, he was occupied with the distillation of benzene on a somewhat large scale for the Paris Exhibition, when the liquid in the retort boiled over and took fire, burning him so severely that he died a few days after.

Benzene was formerly considered to be exclusively found in coal-tar, but this is erroneous. Thus Markownikoff (*Chem. Zeit.*, 1902, p. 572; comp. also the footnote on p. 222) found it in Caucasian petroleum. This was confirmed by Kraemer and Böttcher (*Berl. Ber.*, 1887, p. 601). Graefe (*Chem. Zentr.*, 1906, i., 1681) found as much as 23 g. per cbm. in the gases produced in the destructive distillation of Thuringian lignite. It occurs also in large quantities in petroleum from East India. E. A. Starke took out an American patent, No. 913780 in 1906, for obtaining it from petroleum by means of forming a sulphonic acid.

Mansfield had already utilized the property possessed by benzene. (first observed by Faraday), of crystallizing at 0°, for

<sup>1</sup> *Monit. Scient.*, 1865, p. 446.

<sup>2</sup> *Ann. Chem. Pharm.*, liv., p. 204.

<sup>3</sup> B. P. No. 11260, of Nov. 11, 1847; *Q. J. Chem. Soc.*, i., p. 244.

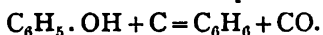
<sup>4</sup> Lecture at the Royal Institution, April 27, 1849.

<sup>5</sup> *Monit. Scient.*, 1870, vol. ii., p. 829.



preparing it in a state of perfect purity. It is allowed to solidify in a freezing mixture; the liquid portion is pressed out; and, if necessary, the operation is repeated. Hofmann<sup>1</sup> has shown that the crystals easily enclose mother-liquor, which causes the product to contain toluene. Hence he prescribed preventing the formation of large crystals and completely separating the mother-liquor by atmospheric pressure, for which purpose he described a convenient laboratory apparatus.

*Formation of Benzene.*—Benzene is formed, on the one hand, by synthesis (condensation) from acetylene and other fatty compounds of simpler molecular constitution, and, on the other, by the splitting-up of more complex compounds, both fatty and aromatic, in both cases by the action of strong heat. In sealed tubes it remains unchanged even when heated to 400° C. Hence it is one of the most stable organic compounds; but on passing through red-hot tubes it is decomposed with formation of more highly condensed hydrocarbons, especially diphenyl (Berthelot, Schulze,<sup>2</sup> Schmidt,<sup>3</sup> Behr und van Dorp).<sup>4</sup> According to M'Kee (*J. Soc. Chem. Ind.*, 1904, p. 403) it begins to decompose at 438°, and at 700° C. it is already strongly dissociated. Passed through red-hot tubes together with ethylene, it yields styrolene, naphthalene, diphenyl, acenaphthene, anthracene, etc. (Berthelot), all of which must consequently be found in crude illuminating-gas and the tar therefrom. Watson Smith (*Chem. Ind.*, 1891, p. 77) observed its formation by the action of carbon on phenol:



C. B. Jacobs (U.S. P. 635017, of 1899) prepares benzol synthetically by heating a mixture of finely powdered metallic carbide and a fusible metallic hydroxide in equivalent molecular weights up to the fusion of the hydroxide, and condensing the evolved hydrocarbons in a receiver.

Scholvien (Fr. P. 347862, 1904) proposes to prepare benzene, its homologues and hydroxyl derivatives, by electrolysis. When coal, tar, tar-oils, or other carbon compounds are exposed to a direct electrical current in a porous cell, or to an alternating electric current in any sort of vessel in the presence of water and soluble or insoluble acids, bases or salts, inorganic or

<sup>1</sup> *Ber.*, 1871, p. 162.

<sup>2</sup> *Annalen*, clxxiv., p. 201.

<sup>3</sup> *Berl. Ber.*, 1874, p. 1365.

<sup>4</sup> *Ibid.*, 1873, p. 727.

organic, first benzene and its homologues and subsequently their hydroxyl compounds are formed. Only very weak currents are required for the reaction, and the temperature has but little influence on the process.

*Properties.*—Benzene is a colourless mobile liquid of peculiar smell. Its boiling-point is stated at  $80^{\circ}$  to  $81^{\circ}$  (Mansfield),  $80^{\circ}\cdot 4$  at a pressure of 760 mm. (Kopp),  $80^{\circ}\cdot 1$  (Warren),  $80^{\circ}\cdot 36$  (Regnault)  $80^{\circ}\cdot 5$  (Weger). Adrieenz (*Berl. Ber.*, 1873, p. 441) found that benzene prepared from tar boils at  $80^{\circ}\cdot 53$  to  $80^{\circ}\cdot 62$ , that from benzoic acid at  $80^{\circ}\cdot 60$  to  $80^{\circ}\cdot 67$ . The temperature of a boiling mixture of benzene and water is  $68^{\circ}\cdot 5$ , that of the mixed vapours  $69^{\circ}\cdot 1$  (Naumann, *Berl. Ber.*, 1877, p. 142). The vapour tensions of benzene and its homologues have been minutely investigated by Woringer (*Chem. Zentr.*, 1900, ii., p. 531). At  $0^{\circ}$  it solidifies to a mass of crystals, which fuse at  $4^{\circ}\cdot 45$  (Regnault) or  $7^{\circ}$  (Mitscherlich). Richards and Shipley (*J. Amer. Chem. Soc.*, 1914, xxxvi., p. 1825) found the freezing-point of absolutely pure benzene, both of that obtained from coal-tar and that synthetically prepared from benzoic acid =  $5\cdot 483 \pm 0\cdot 002^{\circ}$ . The crystals are orthorhombic prisms, whose axes  $a : b : c$  have the ratio  $0\cdot 891 : 1 : 0\cdot 799$  (Groth, *Pogg. Ann.*, cxli., p. 31). Its specific gravity was found at  $0^{\circ} = 0\cdot 8991$  Kopp), at  $15^{\circ} = 0\cdot 884$  (Mendelejeff); at  $0^{\circ} = 0\cdot 8957$ , at  $15^{\circ} = 0\cdot 8820$  (Warren), at  $15^{\circ} = 0\cdot 885$  (Weger). Its coefficient of expansion is stated by Kopp for the temperature  $t^{\circ}$  (between  $11^{\circ}\cdot 4$  and  $81^{\circ}\cdot 4$ ) to be

$$V_t = 1 + 0\cdot 001171626t + 0\cdot 00000127755t^2 + 0\cdot 000000080648t^3.$$

Adrieenz gives the following table for the specific gravity of benzene (prepared from benzoic acid) at various temperatures:—

Temp.	Spec. grav.	Volume.	Temp.	Spec. grav.	Volume.
Degrees.			Degrees.		
0	0·90023	1	45	0·85291	1·05550
5	0·89502	1·00582	50	0·84748	1·06228
10	0·88982	1·01169	55	0·84198	1·06924
15	0·88462	1·01764	60	0·83642	1·07637
20	0·87940	1·02367	65	0·83078	1·08370
25	0·87417	1·02979	70	0·82505	1·09123
30	0·86891	1·03603	75	0·81923	1·09898
35	0·86362	1·04238	80	0·81331	1·10696
40	0·85829	1·04887			

The specific gravity of benzene from tar-oil he found at 0 = 0.90122 and 0.90129.

The volume-weights of benzene at various temperatures are treated in detail by Biron (*Chem. Zentr.*, 1910, i., p. 1912).

The specific heat of benzene between 19° and 46° is 0.450 (Kopp). Its refraction-index<sup>1</sup> for the line A is 1.4593; for D it is 1.5050; and for H, 1.5307; Adrieenz (*loc. cit.*) gives 1.4957 at 15°·2 for D. The molecular combustion-heat of benzene, at constant pressure, is = 779.5 calories;<sup>2</sup> its capillary constant at 15° = 83.65 mm.<sup>3</sup>

Special investigations on the inflaming-points of benzene and other hydrocarbons have been made by Raikow (*Chem. Zeit.*, 1899, p. 145); Meunier (*ibid.*, 1900, p. 951); Holde (*Chem. Zentr.*, 1899, ii., p. 546).

Microchemical investigations on benzene and the other coal-tar hydrocarbons have been made by Behrens (*Chem. Zentr.*, 1901, i., p. 796).

We also mention the work of Kraemer and Spilker on distillation under pressure (*Ber.*, 1900, p. 2205); on the reactions of benzol by W. Loeb (*Ber.*, 1901, p. 915), by Dimroth (*Pharm. Zeit.*, 1901, p. 302), by Sabatier and Senderens (*Chem. Zentr.*, 1901, i., pp. 501, 817).

Benzene is not merely a most important substance for industrial purposes, but even more so for theoretical chemistry. The enormous array of aromatic compounds are all derived from benzene. It would appear almost impossible to find one's way through this interminable field, had not Kekulé's celebrated theory of the constitution of benzene brought light and order into it. It can be stated, without fear of contradiction, that without Kekulé's hexagon formula nothing like so many and so important aromatic compounds would have been discovered as there have been; his hypothesis is certainly one of the most fertile and suggestive that have ever been propounded in Chemistry.

Nearly all chemists agree with Kekulé in assuming that the six carbon atoms of benzene are united in a closed chain (nucleus), and that, of the four bonds of each atom, three are

<sup>1</sup> Gladstone, *J. Chem. Soc.*, 1870, vol. xxiii., p. 152.

<sup>2</sup> Stohmann, Kleber, and Langbein, *Berl. Ber.* (Ref.), 1889, p. 527.

<sup>3</sup> Cohen, *Chem. News*, 1886, vol. liv., p. 306.

satisfied by other carbon atoms of the same nucleus, the fourth being satisfied by hydrogen atoms. But opinions differ as to the special kind of bond ; and it does not seem appropriate here to enter into this theoretical discussion, which is not yet closed.

For the sake of simplicity, benzene is usually represented merely by the figure of a hexagon, and its derivatives by attaching the respective groups to the corners, whilst the empty corners are understood to be filled with hydrogen atoms.

Benzene is very little soluble in water, but sufficiently so to communicate its smell to it. On the other hand, it dissolves a little water: according to Groschuff (*Z. angew. Chem.*, 1911, p. 1451), 0.051 per cent. at 18°. According to Young and Fortey (*ibid.*, 1902, p. 516), nearly all alcohols of low boiling-point, except isoamylic alcohol, form with benzol mixtures of constant boiling-points. Ethylic alcohol, isopropylic alcohol, *n*-propylic alcohol, and tertiary butylic alcohol, form with benzene and water ternary mixtures of constant boiling-point.

Benzene is easily soluble in alcohol, ether, wood-spirit, acetone, etc. It dissolves iodine, sulphur,<sup>1</sup> phosphorus (when hot), and (very easily) fats, ethereal oils, rosins, etc. It is easily inflammable, as well as its vapour, which necessitates great precaution in storing it in quantity. It burns with a strongly smoking flame. Ordinary coal-gas passed through benzene gains very much in illuminating power ; Berthelot even ascribes that of (Paris) illuminating-gas principally to the benzene contained in it; whilst formerly substances of the ethylene series received the credit. This has been confirmed by the researches of Frankland, of Knublauch,<sup>2</sup> etc., and is now pretty generally assumed to be correct. Even atmospheric air passed through benzene yields a mixture burning with a bright flame, upon which property Mansfield at that time (before the discovery of the aniline colours) founded his hopes of an industrial utilization of benzene. Frankland and Thorne<sup>3</sup> made a quantitative investigation of the illuminating power of benzene when mixed in the state of vapour with non-luminous gases.

<sup>1</sup> The somewhat considerable solubility of sulphur in benzene and ether (also the heavy tar-oils) has been studied in detail by E. Pelouze, junior (*Comptes rend.*, lxxviii., p. 1179, lxix, p. 56).

<sup>2</sup> *Ber.*, 1881, p. 240.

<sup>3</sup> *Chem. News*, xxxvii., pp. 36, 72.

Benzene, on being inspired in breathing, causes first a quickening of the pulse and the respiration, afterwards stupefaction, and in large doses (*e.g.* 50 g. for a cat) it produces death. A case of this kind is reported in *Chem. Zeit. Rep.*, 1908, p. 39). In the case of men, the inspiration of 10 g. benzene causes headache, giddiness, inclination to vomiting, coughing, and sleepiness. Forty to 50 g. produce anæsthesia, similar to that produced by chloroform, with violent perspiration, sometimes with all the appearances of drunkenness. The workmen often complain of "ant-creeping" and dryness of the skin, owing to the oily secretions of the skin being dissolved. Such a case is reported in *Chem. Zeit. Rep.*, 1908, p. 39. Nevertheless the men working in india-rubber works, and continually exposed to benzene vapours, enjoy normal health.

There are some contradictions on the point of the toxic quality of the tar hydrocarbons. Berthelot (*Comptes rend.*, cxxxvii., p. 953; *Chem. Zentr.*, 1904, i., p. 527) asserts that benzene, toluene, and xylene have very poisonous effects, whilst naphthalene has not. But Staehelin (*Chem. News*, lxxxix., p. 74; *Chem. Zentr.*, 1904, i., p. 1024) contends that only the vapours of benzene, not those of toluene or xylene, by themselves cause death, and that traces of such vapours form the principal poisonous constituent of coal-gas.

At the second International Congress for Industrial Diseases, Rambousek<sup>1</sup> made a detailed report on industrial benzol poisonings. He enumerates a list of cases of poisonings by benzol, reported in technical publications during the last few years, which occurred in benzol factories, tar distilleries, extraction works, india-rubber factories, and in working with benzol-containing paints, which partly led to transient intoxicating effects, partly to death, but were all of them due to inhalation of the vapour of technical benzol of various qualities.

Lewin (*Z. für Gewerbehygiene*, 1907, p. 528) observed that, if air is slowly passed through benzol and then into a bell-jar in which animals were confined, already after four to six minutes paralysis of the movements, convulsions and loss of consciousness set in, but no after-effects were observed. Santesson (*Skand. Arch. f. Physiol.*, 1900, pp. 1 *et seq.*) also effected

<sup>1</sup> *Concordia*, 1910, p. 448.

chronical infections of animals by inhalations of benzol; these effects were the same both with factory benzols and with pure benzene. Subcutaneous injection of two or three cubic centimetres of benzol per day, in the case of rabbits, led to death within from four to eight days by fatty degeneration of the liver, etc.

Wojciechowski<sup>1</sup> obtained quite similar results.

*Chemical Behaviour of Benzene.*—The changes undergone by benzene when passed through red-hot tubes have been mentioned above (p. 226).

Concentrated sulphuric acid at the ordinary temperature acts very little upon benzene, for which reason the latter can be purified by treatment with that acid. Even then, ordinary benzene contains some thiophen (see below), which can be removed by more energetically agitating with strong sulphuric acid till the "indophenine reaction"—that is, a blue colour imparted to isatin—is no longer obtained (V. Meyer). But on heating the mixture, benzene-monosulphonic acid ( $C_6H_5SO_3H$ ) is formed, and at very high temperatures, or more easily by fuming sulphuric acid, benzene-disulphonic acid ( $C_6H_4(SO_3H)_2$ ). Concentrated nitric acid converts benzene into nitro-compounds, mono- and dinitrobenzene, upon which its detection, its estimation, and, to a great extent, its industrial application are based. Oxidizing reagents, such as potassium permanganate, manganese dioxide, chromic acid, etc., acts upon it but little, and with formation of complex products. About the action of ozone, see below. Chlorine and bromine yield with it addition and substitution products. The action of fuming hydriodic acid under pressure furnishes hexahydrobenzene.

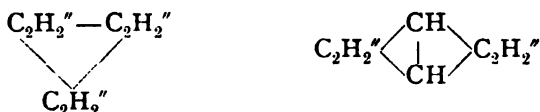
Benzene is a good indicator in iodometry, better than starch; cf. Schwerow (*Chem. Zentr.*, 1905, i., 1046), and Margosches (*ibid.*, ii., 510). It dissolves the iodine with strong red coloration already on adding 2 c.c. of 1/10,000 normal solution to 10 c.c. water, and 5 c.c. benzene, whereas with the same quantity of water and 5 c.c. starch paste, the addition of 5 or 6 c.c. of the above solution is required to produce a faint purple colour.

Benzene, like all aromatic hydrocarbons, is not insensible to atmospheric oxygen, but there ensue autoxidations which, as reported by Weger (*Berl. Ber.*, xxxvi., p. 309) are most easily

<sup>1</sup> Inaug. Diss., Würzburg.

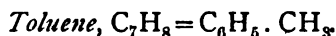
proved by the sulphuric-acid reaction (see below). A still stronger reaction is produced on benzene and its congeners by ozone. If ozone is passed through benzene, the escaping vapours have a strongly acid reaction; *cf.* Houzeau and Renard (*Comptes rend.*, lxxvi., p. 172) and Leeds (*Berl. Ber.*, xvi., p. 975). According to Harries and Weiss (*ibid.*, 1904, p. 3431), in this case a fearfully explosive compound is formed, to which they have given the name "ozobenzol."

Kraemer and Spilker (*Berl. Ber.*, xxxvi., p. 309), looking at the existence of phenanthrene and anthracene, hold it not to be excluded that another benzene exists. Which of two benzenes possible, represented by the graphical formulæ



belongs to the benzene hitherto known, cannot be as yet declared with certainty (*cf.* below).

The methods for estimating benzene vapour in coal-gas have been described (pp. 85 *et seq.*); those for testing liquid benzene will be described in Chapter XI.



*Syn.* methylbenzene. Toluene was discovered, in 1838, by Pelletier and Walter, in the condensation-products from the manufacture of rosin-gas, and was called "retinaphtha." Afterwards Deville obtained it by destructive distillation of tolu-balsam; the name of toluene (toluol) was given to it by Berzelius. Mansfield (*Chem. Soc. Quart. J.*, i., p. 244) found it in coal-tar, and it has since been met with in many mineral oils, *e.g.* in petroleum by Charitschkoff (*Chem. Zeit. Rep.*, 1902, p. 179). Its formation, together with that of analogous compounds, has been mentioned above. It is obtained from coal-tar in very large quantities, and if necessary in a state of great purity, and is largely employed, partly for the manufacture of colouring matters, partly as a solvent. It is more difficult to prepare in a perfectly pure state than benzene, because it does not crystallize.

Our present chemical theories admit only one toluene; and

in fact it has been proved by Berthelot<sup>1</sup> and Rosenstiehl<sup>2</sup> that all toluenes, whatever be their origin, are identical.

Toluene is a colourless, mobile, strongly refractive liquid. Its boiling-point is 110° (Wilson), or 111° (Wilbrand and Beilstein), or 110°·3 (Warren). It solidifies at -90° (Weger). Its specific gravity at 0° = 0·8824, at 15° = 0·8720 (Warren); or at 0° = 0·8841, at 15° = 8702 (Louguinine). The latter states its volume at the temperature  $t$ , if at 0° = 1, as

$$V_t = 1 + 0.001028t + 0.000001779t^2.$$

Deville gives 1·4899 as its refraction-index. The capillary constant at 15° is = 83·95 mm. (Cohen, *Chem. News*, liv., p. 306).

The smell of toluene is slightly different from that of benzene. It is insoluble in water, but communicates its smell to it; it is miscible with alcohol, ether, carbon bisulphide, etc. It dissolves sulphur, phosphorus, iodine, fats, etc. When ignited, it burns with a bright and strongly smoking flame. Passed through red-hot tubes it yields benzene, naphthalene, anthracene, phenanthrene, etc.

According to Berthelot, toluene possesses, similarly to oil of turpentine, the property of rendering oxygen active; when toluene is shaken up with a very dilute tepid solution of indigo in the presence of air, decolorization takes place. According to Weger, in the autoxidation of toluene by atmospheric oxygen, among other substances also benzoic acid is formed.

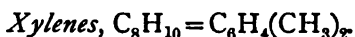
Concentrated sulphuric acid dissolves toluene on heating and prolonged shaking; fuming acid does so much more quickly. Thereby two isomeric sulphonic acids are formed. Nitric acid of less than 1·42 sp. gr. does not act upon it when cold; but fuming nitric acid does so violently, even more so than upon benzene, nitro-products up to trinitrotoluene being formed. Oxidizing agents (dilute nitric acid, chromic acid, potassium permanganate) convert it into benzoic acid, but only with difficulty and great loss, so that this direct oxidation is scarcely practised on an industrial scale. By plumbic oxide toluene at a temperature below 335° is converted into benzene:  $C_6H_5(CH_3) + 3PbO = 3Pb + C_6H_6 + H_2O + CO_2$  (Vincent, *Comptes rend.*, cx., p. 907).

*Hydrotoluenes* up to now have not been found in coal-tar.

<sup>1</sup> *Bull. Soc. Chim.*, 1869, xi., p. 381.

<sup>2</sup> *Ibid.*, xi., p. 385.





*Syn.* dimethylbenzene. Xylene (*i.e.* a mixture of the isomers) was discovered in 1850, by Cahours, in crude wood-naphtha. In coal-tar it was found by Ritthausen and Church; by Mabery in Californian crude petroleum. It has been synthetically produced by Friedel and Crafts, by treating benzene or toluene with methylic chloride in the presence of aluminium chloride.

The xylene of coal-tar, even when entirely separated from its homologues, still showed very different properties in the hands of various observers. Commercial xylol has a boiling-point of  $138^\circ$  to  $140^\circ$ , and at  $0^\circ$  a specific gravity of 0.877. According to Louguinine, its volume between  $0^\circ$  and  $100^\circ$  is found by the formula:  $V_t = 1 + 0.0009506t + 0.000001632t^2$ . If steam is injected into xylol, it is carried away. The mixed vapours have a temperature of  $91.5^\circ$ , and contain upon 100 parts xylene 45 parts water, independently of the shape of the vessel and the speed of distillation (Naumann, *Berl. Ber.*, 1877, p. 1726). Its inflaming-point is about  $21^\circ$ .

Fittig first proved in 1869 (Liebig's *Annalen*, cliii., p. 265) that coal-tar xylol is not a homogeneous body; he stated it to contain 90 per cent. metaxylene and 10 paraxylene. But O. Jacobsen (*ibid.*, cliii., p. 265) has proved the presence of orthoxylene, and estimates the proportions at 70 to 75 per cent. metaxylene, 20 to 25 paraxylene, and 10 to 16 orthoxylene; in any case, different tars differ in this respect (*cf.* Chapter XI.).

*Crude* xylol—that is, such which has not been treated with sulphuric acid (by which considerable quantities of orthoxylene are dissolved)—probably contains much more orthoxylene than was found by Jacobsen in the refined article analyzed by him. This supposition (suggested by me in the first edition of this work, p. 44) has been confirmed by Jacobsen (*Berl. Ber.*, 1881, p. 2628), who found up to 25 per cent. of orthoxylene in crude coal-tar xylene. In the purest state (*i.e.* when 90 per cent. pass over within  $3.6^\circ$  and 95 per cent. within  $4.5^\circ$ ) it consists of 60 per cent. *m*-xylene, 10 to 25 per cent. *o*-xylene and *p*-xylene, and small quantities of trimethylbenzenes, paraffin, and thioxene (Weger).

*Orthoxylene*,  $C_6H_4 \begin{array}{c} \text{---CH}_3 \\ \text{---CH}_3 \end{array} \begin{array}{c} (1) \\ (2) \end{array}$ , is a colourless liquid, whose

pleasant aromatic smell differs from that of its isomers. It boils at  $141^{\circ}$  to  $142^{\circ}$ , and is not yet solid at  $-22^{\circ}$ . It dissolves in concentrated sulphuric acid, forming only one sulphonic acid. Dilute nitric acid forms orthotoluylic acid, fusing at  $102^{\circ}$ ; potassium permanganate forms phthalic acid; chromic acid entirely destroys it by oxidation. The sulphochloride melts at  $52^{\circ}$ , the sulphamide at  $144^{\circ}$ . Capillary constant =  $86.95$  mm. at  $15^{\circ}$  (Cohen).

*Metaxylene* (*syn.* isoxylene),  $C_6H_4 \begin{smallmatrix} \text{---CH}_3 & (1) \\ \text{---CH}_3 & (3) \end{smallmatrix}$ , boils at  $139^{\circ}$ , is also soluble in concentrated sulphuric acid, two sulphonic acids being formed. Dilute nitric acid forms metatoluylic acid, of  $106^{\circ}$  fusing-point; potassium permanganate and chromic acid form isophthalic acid. There are two sulphochlorides, one melting at  $34^{\circ}$ , the other liquid at ordinary temperatures; the two sulphamides melt at  $137^{\circ}$  and  $96^{\circ}$  respectively. Specific gravity of metaxylene =  $0.8668$  at  $19^{\circ}$ . Capillary constant at  $15\frac{1}{4}^{\circ}$  =  $94.3$  mm. (Cohen).

*Paraxylene*,  $C_6H_4 \begin{smallmatrix} \text{---CH}_3 & (1) \\ \text{---CH}_3 & (4) \end{smallmatrix}$ , melts at  $15^{\circ}$ , and boils at  $138^{\circ}.5$  (Weger). It possesses an odour similar to that of orthoxylene, but with a faint smell of aniseed superadded. According to Glinzer and Fittig, sp. gr. (of not quite pure paraxylene) at  $18^{\circ}.5$  =  $0.8625$ . Capillary constant at  $15\frac{1}{4}^{\circ}$  =  $83.80$ . It is very little acted upon even by hot concentrated sulphuric acid; but faintly fuming oil of vitrol dissolves it, forming a sulphonic acid which can be precipitated by water and purified by recrystallization, and from which by dry distillation pure paraxylene is regenerated. This behaviour shows how it can be isolated. Dilute nitric acid forms paratoluylic acid, melting at  $178^{\circ}$ ; potassium permanganate and chromic acid form terephthalic acid. The sulphochloride melts at  $26^{\circ}$ , the sulphamide at  $148^{\circ}$ .

The three isomers dissolved in sulphuric acid can be separated in the following way (Jacobsen). As much as possible of the excess of sulphuric acid is removed by calcium carbonate; the liquid is mixed with a slight excess of sodium carbonate, and the filtrate evaporated so far that on cooling a considerable crop of salt is obtained. This sodium orthoxylene-sulphonate can be purified by recrystallization, whilst the mother-liquors contain sodium metaxylene sulphonate. From these salts the

hydrocarbons are obtained by destructive distillation or by heating with hydrochloric acid to  $195^{\circ}$ . Coal-tar xylene contains a body similar to paraffin, insoluble even in fuming oil of vitriol, which has been examined by Kraemer and Böttcher (*Ber.*, 1887, xx., p. 602) (*cf.* Levinstein's process in the tenth chapter).



Mansfield in 1848 discovered hydrocarbons of the empirical formula  $C_9H_{12}$  in coal-tar, but evidently did not isolate them in the pure state. Like him, other chemists for a number of years believed they had to deal with a homogeneous substance, identical with the retinyl obtained in 1837 by Pelletier and Walter from rosin-oil or cumene (cumol-propylbenzene), and produced by Gerhardt and Cahours from cuminic acid. Even xylene was frequently confounded with cumene. To this confusion Beilstein<sup>1</sup> put an end by describing the hydrocarbon, separated from its homologues as *pseudocumene*. Already Warren<sup>2</sup> had obtained it in a similar state, boiling at  $169^{\circ}.8$ . But Fittig and his disciples<sup>3</sup> proved that Beilstein's pseudocumene is a mixture of two isomeric trimethylbenzenes, viz., of pseudocumene as at present understood (1, 2, 4), and of mesitylene (1, 3, 5). K. E. Schulze (*Berl. Ber.*, 1887, p. 409) found in the fraction of neutral coal-tar oils boiling between  $170^{\circ}$  and  $210^{\circ}$  about 15 per cent. trimethylbenzenes. Besides them O. Jacobsen<sup>4</sup> has found a paraffin,  $C_{10}H_{22}$ , boiling at  $170^{\circ}$  to  $171^{\circ}$ . The same chemist has described<sup>5</sup> the preparation of both hydrocarbons in a pure state by converting them into their sulphamides, separating these by crystallizing from alcohol, and decomposing the sulphamides by heating them with hydrochloric acid to  $175^{\circ}$  (a process too expensive for technical application).

Engler<sup>6</sup> has found both pseudocumene and mesitylene in different kinds of petroleum; so has Markownikoff (p. 222, footnote). The more recent researches in this direction have been made by Weger<sup>7</sup> and G. Schulz.<sup>8</sup>

<sup>1</sup> *Ann. Chem. Pharm.*, cxxxiii., p. 32.

<sup>2</sup> *Chem. News*, xii., p. 292.

<sup>3</sup> *Ann. Chem. Pharm.*, cxxxix., p. 184; cxlv., p. 137; cl., pp. 257, 283, 292.

<sup>4</sup> *Annalen*, clxxxiv., p. 179. <sup>5</sup> *Ber.*, 1876, p. 256. <sup>6</sup> *Ibid.*, 1885, p. 2234.

<sup>7</sup> *Z. angew. Chem.*, 1909, p. 341.

<sup>8</sup> *Berl. Ber.*, 1909, p. 3602.

*Pseudocumene*,  $C_6H_5 \begin{Bmatrix} CH_3 (1) \\ CH_3 (2) \\ CH_3 (4) \end{Bmatrix}$ , boils at  $169^{\circ}.8$  (Weger). Its

smell differs from that of the lower homologues. It is insoluble in water, soluble in ether and alcohol, also in glacial acetic acid (like mesitylene). In sulphuric acid it dissolves (like mesitylene) with formation of a sulphonic acid. Sp. gr. 0.888 at  $15^{\circ}$ . It is more easily prepared in a pure state from the "solvent naphtha" of coal-tar than any other hydrocarbon.

*Mesitylene*,  $C_6H_3 \begin{Bmatrix} CH_3 (1) \\ CH_3 (3) \\ CH_3 (5) \end{Bmatrix}$ , was discovered by Kane<sup>1</sup> by

treating acetone with sulphuric acid. Fittig found it in coal-tar oil; smells rather like garlic. Boiling-point (corr.) at  $164^{\circ}.5$  (Weger); sp. gr. 0.865 at  $15^{\circ}$ . According to K. E. Schulze (*Berl. Ber.*, 1877, p. 410), it is the most prevalent of the three trimethylbenzenes in coal-tar.

*Hemellithol*,  $C_6H_3 \begin{Bmatrix} CH_3 (1) \\ CH_3 (2) \\ CH_3 (3) \end{Bmatrix}$ , discovered by O. Jacobsen in

1882 (*Berl. Ber.*, 1882, p. 1857), and found by him in coal-tar oils in 1886 (*ibid.*, 1886, p. 2517); also by Krömer (*ibid.*, 1891, p. 2407) in commercial pseudocumidine. Boils at  $175^{\circ}$ , and does not solidify at  $-20^{\circ}$ ; sp. gr. 0.901 at  $15^{\circ}$ .

Weger<sup>2</sup> has found that cumene, and many other unsaturated hydrocarbons in coal-tar, absorb oxygen from atmospheric air when kept in daylight; they then burn with a yellow flame, and otherwise change their properties.

*Ethylbenzene*,  $C_6H_5 \cdot C_2H_5$ .

This isomer of the xylenes has been found in technical coal-tar xylene by Noelting and Palmer<sup>3</sup> to the extent of 10 per cent., as the first representative among coal-tar oils of hydrocarbons with a prolonged lateral chain. Kraemer (priv. comm.) points out that ethylbenzene does not exist as such in coal-tar, no more than any other hydrocarbons with prolonged lateral chains, because these are split off during the heating in the tar-still. The ethylbenzene found by Noelting and Palmer

<sup>1</sup> *Poggend. Ann.*, xliv., p. 474.

<sup>2</sup> *Berl. Ber.*, 1903, 309.

<sup>3</sup> *Berl. Ber.*, 1891, p. 1955; *Z. Angew. Chem.*, 1909, p. 341.

must have been formed as secondary product from the paracumarone contained in the crude xylenes, *washed with strong sulphuric acid* from which the "technical xylene" had been obtained by distillation. Moschner (*Berl. Ber.*, xxxiv., p. 1261) in working up tar xylene for pure xylenes obtained after removing the *p*-xylene as much as possible from the respective fraction, from each 100 kg. crude xylene about 4 kg. of the ethylbenzenes sulphonate of soda, crystallizing in flexible needles, shining like fat. By decomposing that sulphonic acid by water under pressure, the hydrocarbon is obtained in a pure form. It has been synthetically prepared by Brochet.<sup>1</sup> Colourless liquid, smelling like xylene; boiling-point 137°. Friedel and Crafts<sup>2</sup> describe a method for separating it from the benzol by the bromine derivatives. The pentabromide of ethylbenzene appears in fine crystals; fusing-point 137° (Weger).

According to Weger, this hydrocarbon is very difficult to isolate from the coal-tar distillates, so that it is more expensive than the synthetically produced substance.

*Cumenes*,  $C_9H_{12}$ .

Schultz, Perl, and Szekely (*Berl. Ber.*, 1909, p. 3616) have proved the presence of both cumene proper (isopropylbenzene) and of normal propylbenzene in solvent naphtha.

*Ethyltoluenes*,  $C_9H_{14}$ .

Schultz and Perl (*ibid.*) have found all three ethyltoluenes (*o*, *m*, and *p*) in solvent naphtha.

*Cymene* (*Propylmethylbenzene*),  $C_{10}H_{14}$ .

has been found in coal-tar by Berthelot. Boils at 180°. Cf. also Rommier (*Jahresb.*, 1873, p. 368).

*Tetramethylbenzenes*,  $C_{10}H_{14} = C_6H_2(CH_3)_4$ .

K. E. Schulze<sup>3</sup> found the 1, 2, 4, 5 *durene* in the fraction of tar-oil boiling between 180° and 200°, after removing the bases and phenols. White scales, with a faint fluorescence, smelling

<sup>1</sup> *Comptes rend.*, cxvii., p. 115.

<sup>2</sup> *Ibid.*, ci., p. 1218.

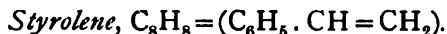
<sup>3</sup> *Ber.*, 1885, p. 3032.

similar to pseudocumene; fusing-point  $80^{\circ}$  to  $81^{\circ}$ ; boils at  $196^{\circ}$ ; sublimes with much more difficulty than naphthalene. Most probably other isomers are present in this oil, which occurs in coal-tar in nearly the same proportion as benzene; the isomer 1, 2, 3, 5 even in larger quantity than durene, but the 1, 2, 3, 4 tetramethylbenzene was not found.

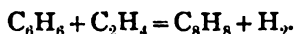
He also obtained from 15 to 20 per cent. of these in the neutral fraction boiling between  $170^{\circ}$  and  $210^{\circ}$ .<sup>1</sup>

### *Naphthenes*

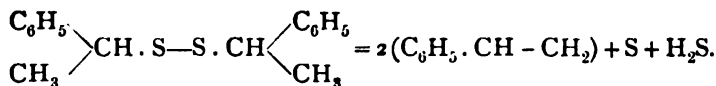
have been proved to occur in coal-tar by Kraemer and Spilker,<sup>2</sup> and in lignite by Heusler.<sup>3</sup> Nononaphthene,  $C_9H_{18}$ , has been found by Ahrens and Modzenski (*Z. angew. Chem.*, 1908, p. 1411) in waste oil from the manufacture of nitroxylenes, and must have existed originally in the coal-tar.



*Syn.* cinnamene, vinylbenzene. Usually obtained from storax or Peru balsam; synthetically by Berthelot<sup>4</sup> by condensation of acetylene at the temperature of softening glass, or better, by passing a mixture of benzene and ethylene through red-hot, and even better, through white-hot tubes, thus:



It is also obtained from  $\alpha$ -ethylphenylmercaptane disulphide quite smoothly, together with a little ethylbenzene and diphenylthiophene:



These and similar reactions explain the occurrence of styrolene in coal-tar, in which, however, it occurs only in insignificant qualities.<sup>5</sup>

It is a colourless mobile oil, with a strong aromatic smell, reminding one of benzene and naphthalene. It does not

<sup>1</sup> *Ber.*, 1887, p. 410.

<sup>2</sup> *Ibid.*, 1887, p. 595.

<sup>3</sup> *Ibid.*, 1895, p. 488.

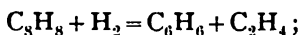
<sup>4</sup> *Comptes rend.*, lxiii, pp. 481, 518, 792, 834; lxviii, p. 327.

<sup>5</sup> Berthelot, *Z. für Chemie*, 1866, 736; Kraemer and Spilker, *Berl. Ber.*, 1890, pp. 3169, 3269.

solidify at  $-20^{\circ}$ , boils at  $145^{\circ}$ , but volatilizes at ordinary temperature, so that it does not leave a grease-spot on paper. Sp. gr. at  $15^{\circ}=0.907$  (Weger). Its solubilities are quite analogous to those of benzene. Caustic potash has no action upon it; fuming sulphuric acid converts it into a sulphonic acid, ordinary sulphuric acid only into a solid polymer, which, on distillation, is partly reconverted into styrolene. Chlorine and bromine unite directly with it. Fuming nitric acid dissolves it, forming a nitro-compound. At a red heat it splits up into benzene and acetylene,



or, if mixed with hydrogen, into benzene and ethylene,



that is, the reaction is the inverse of that which took place in its formation. Heated with ethylene it yields benzene and naphthalene; heated with benzene, naphthalene and anthracene. It probably plays an important part in the formation of these higher hydrocarbons, and, for that very reason, does not occur in large quantities in coal-tar. The investigations of Kronstein (*Ber.*, 1902, pp. 4150, 4153) on the polymerization of styrolene point in the same direction. According to Königs (*Ber.*, 1890, p. 3147), it also condenses easily with phenols. A very complete investigation on styrolene has been made by Klages (*Ber.*, 1902, pp. 2245, 2633).

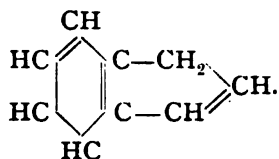
In the presence of sulphuric acid, styrolene forms molecular compounds with toluene, xylene, cumene, etc., which can be distilled without decomposing. On overheating their vapours, methane and hydrogen are split off, and anthracene or its homologues are formed (Kraemer and Spilker).

### *Indene, C<sub>9</sub>H<sub>8</sub>*

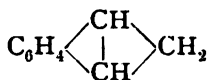
Discovered by Kraemer and Spilker (*Ber.*, 1890, p. 3276) in the fraction of crude benzol boiling at  $176^{\circ}$  to  $182^{\circ}$ , which contains about 20 per cent. of it. In order to obtain it, as much picric acid is dissolved at a higher temperature in that fraction as is required for combining with the unsaturated compounds (previously ascertained by titration), and the solution is allowed to cool down. The picrate crystallizing out easily contains a

According to the German patents No. 205405 and 209694 of the Duisburg Gesellschaft für Teerverwertung, indene can be obtained synthetically by the same process as will be described lower down for fluorene.

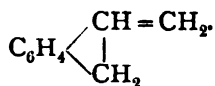
Indene is a colourless liquid, boiling at  $182^{\circ}$ . On standing, it takes a yellowish-green colour, which vanishes in the light. Weyer, when examining a purified substance, found the sp. gr. = 1.008. Spilker and Dombrowsky (*Ber.*, 1909, p. 573) found the boiling-point of really pure indene =  $182^{\circ}.2$  to  $182^{\circ}.4$  at 761 mm. pressure; sp. gr. 1.0002; solidifying point =  $-2^{\circ}$ . Its structural formula proves it to be a link between benzene and naphthalene:



Perhaps other formulæ or isomers must be assumed, as pointed out by W. H. Perkin, jun., and Revay (*Berl. Ber.*, 1893, p. 2251), viz., that possessing the formula :

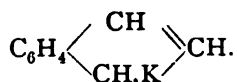


which would show the same chemical behaviour. Dennstedt and Ahrens (*ibid.*, 1895, p. 1331), on account of the great similarity of indene to styrolene, consider it possible that its constitution is:





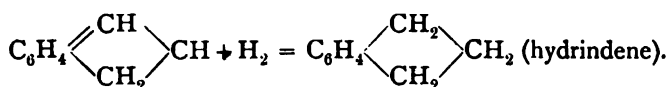
Schultz (*loc. cit.*) takes the formula of indene-potassium to be :



According to Kraemer and Spilker (*loc. cit.*), indene is the cause of certain colorations produced in the treatment of various coal-tar products, *e.g.*, of impure naphthalene with concentrated sulphuric acid, and the red colour produced in phenol by sunlight.

Dennstedt and Ahrens (*Berl. Ber.*, 1894, p. 601) found indene in the condensation product obtained from illuminating gas by cooling down to  $-20^\circ$ .

Indene is easily reduced by nascent hydrogen in its solution in ethylic alcohol, the double binding being split by the entrance of two hydrogen atoms :



### *Hydrindene,*

the formation of which has just been mentioned, has been likewise found in coal-tar by Kraemer and Spilker (*Ber.*, 1896, p. 561).

Special investigations on indene and hydrindene have been made by J. Thiele (*Ber.*, 1900, p. 771), Moschner (*ibid.*, 1900, p. 757), and Weger and Billmann (*Ber.*, 1903, p. 640).

Hydrindene is contained in the heavy coal-tar oils, and can be isolated therefrom. According to Moschner, 2.5 per cent. of it are contained in the cumene fraction. It is, however, more easily obtained from the heavy benzol *resin* (Kraemer and Spilker, *Ber.*, xxxiii., p. 2257) by the action of high temperatures.

It boils at  $176^\circ$  to  $176.5^\circ$ ; sp. gr. 0.957 at  $15^\circ$ . By concentrated sulphuric acid it is not polymerised, but sulphonated.

*Methylindenes and Dimethylindenes.*

*Methylindenes*,  $C_{10}H_{10}$ , and *Dimethylenes*,  $C_{11}H_{12}$ , have been found by Boes (*Chem. Zentr.*, 1902, i., 811), in the fraction of coal-tar boiling at  $220^{\circ}$  to  $230^{\circ}$ . If all six possible dimethylindenes occur in coal-tar, the 4, 6 and 5, 7 isomer must occur in the greatest proportion. (Cf. also *Ber.*, 1902, p. 1762; and *Chem. Zentr.*, 1902, ii., 55.)

*Naphthalene*,  $C_{10}H_8$ .

Discovered by Garden in 1826; first studied in detail by Laurent. It is formed in innumerable cases by the action of heat on organic substances, but only at rather high temperatures; so that tar obtained at a comparatively low heat does not contain it at all. In gas-tar it always occurs, but in greatly varying quantities, very much more abundantly since the cast-iron retorts have been replaced by fireclay retorts worked at much higher temperatures. The statement of Calvert (*Comptes rend.*, xlix, p. 262), that Newcastle tar contains 58 per cent. of naphthalene, is absurd on the face of it; ordinarily tar seldom contains more than from 5 to 10 per cent. The mode of its formation has been explained on p. 226.

Weger (*Z. angew. Chem.*, 1909, p. 338) has observed the formation of naphthalene on passing cyclopentadiene or dicyclopentadiene through a tube kept at a low red heat, hydrogen splitting off:  $2 C_5H_6 = C_{10}H_8 + 2 H_2$ , together with a little benzene and anthracene. This reaction is interesting with respect of the theory of the formation of tar, since it shows the transition from a ring of five carbon atoms to aromatic compounds by the influence of heat.

Naphthalene in the pure state forms white crystalline masses or thin rhomboidal scales; on spontaneous evaporation of an ethereal solution it appears in monoclinic prisms (Laurent). It fuses at  $79^{\circ}$ ; solidifying-point =  $79^{\circ}.6$  to  $79^{\circ}.8$  (Weger, *Z. angew. Chem.*, 1909, p. 341); the statements respecting its boiling-point vary between  $212^{\circ}$  and  $220^{\circ}$ ; but  $218^{\circ}$  seems to be correct. Sp. gr. at  $15^{\circ} = 1.1517$ , at  $18^{\circ} = 1.1508$ , at  $79^{\circ}.2 = 0.9778$ , at  $100^{\circ} = 0.9628$  (compared with water at  $0^{\circ}$ ). Melted naphthalene, according to Vohl,<sup>1</sup> absorbs a large quantity of air, which is

<sup>1</sup> *J. prakt. Chem.*, cii, p. 29.

given off again on cooling; it is said to be much richer in oxygen than atmospheric air. Naphthalene volatilizes far below its boiling-point, and distils both with aqueous vapour and with that of light tar-oils; hence it always appears with the latter in crude tar-oils. In an ammoniacal atmosphere it volatilizes more easily than in air, hydrogen, etc.<sup>1</sup> Even at ordinary temperatures it volatilizes slowly and gives off a penetrating tarry smell, which clings a long time to clothes, etc., and is said to keep off moths and other vermin. Ballo<sup>2</sup> asserts that this smell is not that of pure naphthalene, but of leucoline oil; however, the purest obtainable naphthalene exhales it quite strongly. Justin Mueller, according to *Chem. Zeit.*, 1905, p. 221, in that year communicated to the Société industrielle de Rouen the startling news that naphthalene, when spread in thin layers on glass or stone plates, volatilizes at ordinary temperatures! Its taste is pungent. Edlefoen (*Chem. Zentr.*, 1905, ii., p. 341) describes the action of naphthalene on the human organism when taken in small quantities. It burns with a strongly smoking flame, but its vapour mixed in small quantity with gas considerably enhances the illuminating power of the latter. The heat of combustion of 1 g. naphthalene is 96,356 to 96,683 calories (Fries, *Chem. Zentr.*, 1907, i., p. 510).

It is insoluble in cold<sup>3</sup> but slightly soluble in hot water; so that the latter turns milky on cooling. It is easily soluble in alcohol, ether, fatty and essential oils, and acetic acid, very much so in phenols, but less easily in the indifferent tar-oils. When melted, it dissolves phosphorus, sulphur, indigo, and several metallic sulphides, which crystallize on cooling. According to Bechi,<sup>4</sup> 100 parts of absolute alcohol at 15° dissolve 5.29 parts, at the boiling-point any quantity; 100 parts of toluene at 16° 5, 31.94 parts, at 100° any quantity. The quantitative estimation of naphthalene in coal-gas and in other cases will be described in Chapter IX.

According to J. F. Smith (*J. Soc. Chem. Ind.*, 1902, p. 1225)

<sup>1</sup> Tieftrunk, *Ber.*, 1878, p. 1466.

<sup>2</sup> *Dingl. polyt. J.*, ccii., p. 377.

<sup>3</sup> Lupton (*Chem. News*, xxxiii., p. 90) doubts this, but does not adduce any positive proof to the contrary.

<sup>4</sup> *Berl. Ber.*, 1879, p. 1928.

naphthalene at 15°.5 is dissolved by 100 parts of various solvents in the following proportions:—

Benzene (pure) . . . . .	45.80 parts
Toluene . . . . .	32.00 "
Xylene . . . . .	31.50 "
Cumene . . . . .	30.10 "
Commercial 90 per cent. benzol . . . . .	43.20 "
Solvent naphtha . . . . .	31.72 "
50 benzene + 50 toluene . . . . .	39.80 "
30 " + 70 " . . . . .	37.20 "
50 per cent. commercial benzol . . . . .	31.80 "
Carburine, sp. gr. 0.672 . . . . .	16.90 "
Creosote oil, sp. gr. 1.03 (containing 8 per cent. phenols) . . . . .	9.65 "
Scotch blast-furnace oil, sp. gr. 0.985 (containing 31 per cent. phenols) . . . . .	17.64 "
Heavy tar-oil . . . . .	8.90 "

Alkalis do not act very much upon naphthalene, but alkaline liquors dissolve a little of it. Concentrated sulphuric acid, on heating, converts it into sulphonic acids; below 70° principally into the  $\alpha$ , at 160° almost entirely into the  $\beta$  modification. This behaviour is very important, because the corresponding naphthols can only be made from the proper sulphonic acids. Chlorine yields both addition and substitution products; nitric acid, nitronaphthalene.

According to Fritzsche, naphthalene forms with picric acid the compound,  $C_{10}H_8 + C_6H_3(NO_2)_3O$ , crystallising from ether in golden yellow needles or monoclinic prisms, fusing-point 149°, which are only with difficulty dissolved by boiling water. It forms double compounds also with other nitro-compounds.

The constitution of naphthalene has been elucidated chiefly by the researches of Laurent, later on by Erlenmeyer<sup>1</sup> and Graebe<sup>2</sup>; it is generally assumed to consist of two benzene nuclei, attached to each other by two carbon atoms.

#### *Naphthalene dihydride, $C_{10}H_{10}$*

Discovered by Berthelot<sup>3</sup> as a product of the action of concentrated hydriodic acid on naphthalene; occurs also in coal-tar.

<sup>1</sup> *Ann. Chem. Pharm.*, cxxxvii., p. 246.

<sup>2</sup> *Z. für Chemie*, [2], iv., p. 114.

<sup>3</sup> *Bull. Soc. Chim.*, 1868, ix., p. 287.

A viscid fluid, with a strong, disagreeable smell, boiling at  $200^{\circ}$  to  $210^{\circ}$ , is powerfully acted upon by bromine, and dissolves in cold fuming nitric acid. It has been studied in detail by Bamberger and Lodter.<sup>1</sup>

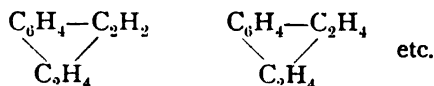
*Naphthalene tetrahydride*,  $C_{10}H_{12}$ ,

occurs in small quantity together with the dihydride; it boils at  $190^{\circ}$ . Its other properties are similar to those of the latter body. Boes (*Chem. Zentr.*, 1902, ii., 1119) found that it absorbs oxygen very easily. He believes it to be identical with a hydrocarbon found by Graebe and Guye (*Ber.*, 1883, xvi., 3028), which absorbs oxygen from atmospheric air.

Kraemer and Spilker (*Berl. Ber.*, 1896, p. 561) isolated this compound from coal-tar.

Bamberger and Bordt (*ibid.*, 1889, p. 631) obtained  $\beta$  naphthalene tetrahydride synthetically by the action of a boiling solution of cupric sulphate on tetrahydronaphthyl hydrazin, as a water-white, fluid oil, intensely smelling of naphthalene, boiling at  $208^{\circ}$  under a pressure of 708 mm.

Kraemer and Böttcher (*ibid.*, 1887, p. 603) consider these substances, found by Berthelot in coal-tar, and by themselves also in petroleum, and to which in any case also belong the substances found by Markownikoff (*supra*, p. 222) in petroleum, of the formulæ  $C_{11}H_{14}$ ,  $C_{11}H_{12}$ ,  $C_{12}H_{14}$ , etc., *not* to be naphthalene hydrides, but give them the formulæ :



In accordance with their annular formulæ they do not add bromine, but owing to the presence of acetylene groups they yield sulphonic acids. It is an argument against their being naphthalene hydrides, that on superheating they do not pass over into naphthalene.

*Methynaphthalenes*,  $C_{11}H_{10}$ .

Reingruber (*Annalen*, ccvi., p. 367) found these in that portion of coal-tar which distils between  $220^{\circ}$  and  $270^{\circ}$ , and which remains liquid at ordinary temperatures; but the two isomeric

<sup>1</sup> *Berl. Ber.*, 1891, p. 1887; 1893, p. 1833.

methylnaphthalenes were only separated by K. E. Schulze (*Ber.*, 1884, p. 842). They are miscible in all proportions with absolute alcohol, ether, benzene, carbon disulphide, and glacial acetic acid. Oxidizing agents act briskly upon them, and destroy them with evolution of carbon dioxide. The two isomers can be separated by means of their sulphonic acids.

Wendt (*Ber.*, 1892, p. 857) separated the two isomers by partial fusion of the frozen mixture. But Wichelhaus (*ibid.*, 1891, p. 3918) objects to this, because the diphenyl, always present, is not removed in this way. The pure hydrocarbons can be only obtained after converting them into picric-acid compounds.

*α* *Methylnaphthalene* is a colourless oil of aromatic smell, with strong refraction and with fluorescence. It solidifies at  $-22^{\circ}$ , and boils at  $240^{\circ}$  to  $243^{\circ}$ ; sp. gr. 1.005 at  $19^{\circ}$ .

*β* *Methylnaphthalene* crystallizes in scales somewhat like naphthalene, of rather pungent smell and burning taste; it melts at  $32^{\circ}.5$ , and boils at  $241^{\circ}$  to  $242^{\circ}$  (Weger).

Both methylnaphthalenes form with two molecules sulphuric acid at ordinary temperatures two isomeric monosulphonic acids which can be separated by means of the differing solubilities of their barium and lead salts.

The ordinary "creosote oil" of trade, which distils mainly between  $200^{\circ}$  and  $300^{\circ}$ , contains about 6 per cent. of these methylnaphthalenes, rather more of the *β* than of the *α* modification.

#### *Dimethylnaphthalene*, $C_{12}H_{12}$

Emmert and Reingruber<sup>1</sup> found a substance of this composition, boiling at  $262^{\circ}$  to  $264^{\circ}$ , in coal-tar. There are evidently several isomeric bodies of this formula, but so far it has not been found practicable to separate them.

Tammann (*Ger. P.* 95597; *Z. angew. Chem.*, 1898, p. 46) has prepared some new di-, tri-, and tetramethylnaphthalenes from petroleum and shale-oil.

#### *Phenylnaphthalenes*, $C_{10}H_{12}$

Most probably these occur in coal-tar, but they have been only synthetically obtained by Moehrlau and Berger (*Berl. Ber.*,

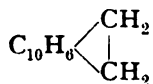
<sup>1</sup> *Annalen*, ccxi., p. 65.

## 248 PROPERTIES OF COAL-TAR AND ITS CONSTITUENTS

1893, p. 1199) and Zincke and Breuer (*ibid.*, 1878, p. 1403). The  $\alpha$  compound is a liquid boiling at  $324^\circ$ , the  $\beta$  compound fuses at  $101^\circ$  to  $102^\circ$ .

### *Acenaphthene*, $C_{12}H_{10}$

according to Weger, occurs in that portion of coal-tar which boils at  $270^\circ$  to  $300^\circ$ , especially between  $280^\circ$  and  $290^\circ$ , and crystallizes on cooling. By recrystallizing from light tar-oil or alcohol, or cautious subliming, it is obtained in the pure state.<sup>1</sup> It fuses at  $95^\circ$  and boils at  $278^\circ$ . Crystallized from alcohol, it forms long, colourless, shining needles; from heavy tar-oils it separates in hard, brittle crystals. Its smell resembles that of naphthalene. It is little soluble in cold, easily in boiling alcohol. Bromine acts readily upon it; concentrated sulphuric acid dissolves it, forming a sulphonic acid, all the salts of which are easily soluble; concentrated nitric acid forms a nitro-compound. Its constitution is—



Acenaphthene, in the shape of quinone, is recently employed for the preparation of remarkably solid "vat-dyes." On being heated with sulphuric acid, it yields trinaphthylbenzene (Rehlander, *Ber.*, xxxvi, p. 1583; Dzwinsky and Bachmann, *ibid.*, pp. 962 and 3768), which probably occurs in coal-tar; on being treated with plumbic oxide it yields acenaphthylene, which likewise probably occurs in coal-tar (Weger).

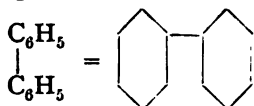
### *Acenaphthene hydride*, $C_{12}H_{12}$

is stated by Berthelot to occur together with the preceding compound in coal-tar. It boils at  $260^\circ$ . A tetrahydride,  $C_{12}H_{14}$ , has been obtained by Bamberger and Lodter synthetically as a colourless syrup, boiling at  $279.5^\circ$  (*Berl. Ber.*, xx., p. 3073). A perhydride,  $C_{12}H_{20}$ , has been obtained by Liebermann and Spiegel (*Ber.*, 1889, p. 779) as a colourless liquid, boiling at  $235^\circ$  to  $236^\circ$ .

<sup>1</sup> Berthelot, *Ann. Chim. Phys.* [4], xii., p. 226.

*Diphenyl*,  $C_{12}H_{10}$ 

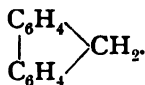
Discovered in 1862 by Fittig.<sup>1</sup> It occurs in that fraction of coal-tar which boils at from  $220^{\circ}$  to  $270^{\circ}$ ; <sup>2</sup> this has been confirmed by K. E. Schulze (*Ber.*, 1885, p. 1203), who considers it also probable that higher homologues (methyldiphenyl) occur there as well. It fuses at  $70^{\circ} \cdot 5$ , and boils at  $254^{\circ}$ . It readily dissolves in alcohol and ether, and crystallizes in large colourless scales. Bromine, sulphuric acid, and nitric acid act upon it, and form corresponding derivatives. Its rational formula is



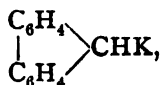
*Diphenyl hydrides* have been prepared by Bamberger and Lodter (*Ber.*, xx., p. 3077).

*Fluorene*,  $C_{13}H_{10}$ 

*Syn.* diphenylene-methane. Prepared by Berthelot (*Comptes rend.*, lxxv., p. 465) from coal-tar, synthetically by Graebe, Fittig, and others in various ways; specially examined by Barbier (*ibid.*, lxxvii., p. 442; lxxix., p. 1151). It is obtained from the fraction of coal-tar boiling between  $290^{\circ}$  and  $350^{\circ}$ , after naphthalene and anthracene have been separated by fractional distillation; the portion distilling between  $295^{\circ}$  and  $310^{\circ}$  is purified by repeated recrystallization from alcohol. It forms colourless scaly crystals with a violet fluorescence, little soluble in cold, easily in hot alcohol, also in ether, benzene, and carbon bisulphide. Fuses at  $116^{\circ}$  (Weger), boils at  $295^{\circ}$ , but volatilizes with aqueous vapour. Bromine and nitric acid yield derivatives with it. The rational formula is



Weissgerber (*Ber.*, 1901, p. 1659) showed that fluorene has a slightly acid character. When fused with caustic potash at  $270^{\circ}$  to  $290^{\circ}$  C., it forms a compound of the formula



<sup>1</sup> *Ann. Chem. Pharm.*, cxxi., p. 361.    <sup>2</sup> Fittig and Büchner, *Ber.*, 1875, p. 22.



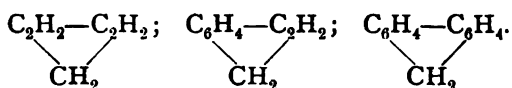
and by this means it can be obtained in the pure state from the high-boiling fractions of coal-tar, as the melt thus formed can be mechanically separated from the non-attacked hydrocarbons, and on being treated with water, is split up into KOH and regenerated fluorene.

The Gesellschaft für Teerverwertung in Duisburg (Ger. Ps. 203312 and 209432) obtains fluorene from mixtures with other substances by transforming it into an alkaline compound which can be separated from unchanged hydrocarbons. This is done by a treatment with sodium, preferably in the presence of a small quantity of organic bases, like aniline, benzylamine, or pyridine, and their homologues, which seem to act as contact substances.

*Indene* (cf. p. 241) is obtained in a similar manner, according to Ger. Ps. 205465 and 209694 of the same firm.

There is a series of isomers of this formula<sup>1</sup> which are probably partly contained in coal-tar; also a perhydride (Liebermann and Spiegel, *vide supra*). Cf. also the investigations of J. Thiele (*Ber.*, 1900, p. 851), and Stoermer and Boes (*ibid.*, 1900, p. 313).

Fluorene forms a natural series with cyclopentadiene and indene:



*γ-Diphenylene methane* possibly also occurs in coal-tar (Hodgkinson and Mathews, *J. Soc. Chem. Ind.*, 1883, i., p. 163). Leaflets with a mother-of-pearl shine, or prismatic needles, fusing at 118°, boiling at 295°.

The *hydrides of fluorene* have not yet been found in coal-tar. They have been described by Guye (*Bull. Soc. Chim.* [3], iv., p. 266); Liebermann and Spiegel (*Berl. Ber.*, xxii., p. 779).

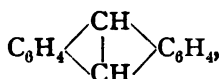
### *Anthracene*, C<sub>14</sub>H<sub>10</sub>

Discovered by Dumas and Laurent in 1832, and described as *paranaphthalene*; more especially examined in 1857 by Fritzsche, who was the first to find it in coal-tar.<sup>2</sup> This was confirmed by Anderson's extended investigation in 1862.

<sup>1</sup> Carnelley, *J. Chem. Soc.*, Nov. 1880, p. 701; Lunge and Steinkauler, *Ber.*, 1880, p. 1656.

<sup>2</sup> *J. prakt. Chem.*, lxxiii., p. 286.

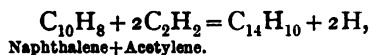
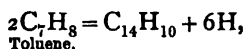
Anderson also established the correct formula of anthracene. Synthetically it was first prepared by Limpricht<sup>1</sup> in 1866, from benzylic chloride, in the same year by Berthelot, pyrogenetically, from simpler hydrocarbons. The most important epoch in its history was marked by Graebe and Liebermann's discovery, in 1868, that it is formed from alizarin by the reducing action of zinc dust, and that alizarin can be synthesized from it.<sup>2</sup> The same chemists established the structural formula of anthracene, but first gave it that now generally ascribed to phenanthrene. Anthracene is now universally represented thus :



*i.e.*, two benzene nuclei, connected by two carbon atoms which are united with each other by another bond. It is also now ascertained that both bonds are in the ortho-position towards the benzene nuclei.

Anthracene is formed in many cases when organic substances are subjected to high temperatures, not merely in the destructive distillation of coal, but also when passing the vapours of petroleum, brown-coal-tar, wood-tar, benzene, spirits of turpentine, etc., through red-hot tubes.

The mode of its formation from other hydrocarbons is illustrated by the following equations, which may serve as examples :—



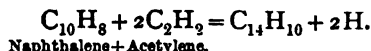
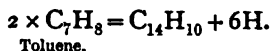
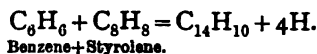
etc., etc.

It has been synthetically obtained from toluene-styrene by Kraemer and Spilker (*Ber.*, 1890, pp. 3169 and 3269); other syntheses are those by Behr and Van Dorp—(*Ber.*, 1874, pp. 578 and 753; 1875, p. 17); Perkin and Hodgkinson (*J. Chem. Soc.*, xxxvii., p. 526); Paternò and Fileti (*Ber.*, 1874, p. 1202); Jackson and White (*Amer. Chem. J.*, ii., p. 283); Anschütz and Eltzbacher (*Ber.*, 1883, p. 623); and Delaire (*ibid.*, 1895, Ref. p. 748).

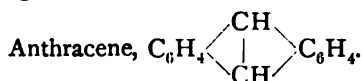
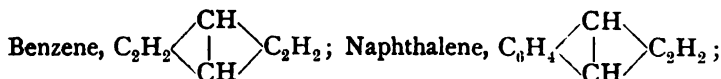
<sup>1</sup> *Ann. Chem. Pharm.*, cxxxix., p. 308.

<sup>2</sup> *Ber.*, 1868, p. 49.

Its formation from other hydrocarbons can be represented by the following equations :—



Note the natural series :—



Köhler<sup>1</sup> found 35 per cent. anthracene in a product accidentally formed by a violent reaction on overheating the higher-boiling fractions of crude carbolic acid, although that product had been obtained from "light oil," and could hardly contain substances which would yield anthracene by a mere splitting-off of the elements of water. He regarded this as a confirmation of K. E. Schulze's theory of the formation of the hydrocarbons of tar from phenols, and also of the statement that the anthracene of coal-tar is for the most part formed during the process of distillation itself; but this view cannot be maintained in face of the smooth synthesis from toluene-styrene by Kraemer and Spilker. Kraemer (priv. comm.) states that the above observation cannot be correct; by overheating phenol mere traces of anthracene are formed. Zmerzlikar (*Z. angew. Chem.*, 1895, p. 468) denies the possibility of the formation of anthracene by the overheating of phenols.

Anthracene has also been found in that peculiar greasy substance called "stupp," which is formed in the distillation of mercury from its ores (G. Goldschmidt and M. von Schmidt).

Its preparation from the highest-boiling constituents of coal-tar, and the analysis of crude anthracene, will be minutely described in a separate chapter later on (Chapter VII.). The preparation of *chemically pure anthracene* (which is not a commercial article) is not easy, unless crude anthracene

<sup>1</sup> *Ber.*, 1885, p. 859.

distilled over caustic potash can be employed. From this, by one washing with carbon disulphide and several recrystallizations from petroleum spirit, pyridine or benzene, beautiful white scales with blue fluorescence are obtained, which it is very difficult to obtain from ordinary crude anthracene. This is best accomplished after subliming this at the lowest possible temperature and washing with ether to remove yellow colouring-matters; or it is dissolved in benzene and bleached by sunlight, in which case a little paranthracene is always formed. The safest way to obtain chemically pure anthracene is to reduce its derivatives by zinc-dust.<sup>1</sup>

Pure anthracene forms shining white scales (clinorhombic prisms) with purple fluorescence. It fuses at 210° (Fritzsche, Berthelot), or 213° (Graebe and Liebermann), or 216°·5 (Reissert, *Ber.*, 1890, p. 2245), and sublims at about the same temperature, with a pungent smell, yielding small, mica-like scales. At about 360° (certainly above phenanthrene) it boils and yields a yellowish-white crystalline distillate; a portion, however, is always decomposed. In the cathode-light vacuum it sublims already at 103° to 104° (Krafft and Weylandt, *Ber.*, 1896, p. 2240).

Pure anthracene is insoluble in water, little soluble in alcohol, more so in ether, benzene, and essential oils, as well as in boiling alcohol, and especially in light tar-oils. According to Gessert,<sup>2</sup> 100 parts of

Alcohol, cold	.	dissolve 0·6 of anthracene
Benzene	.	" 0·9 "
Carbon disulphide	"	1·7 "

According to Versmann,<sup>3</sup> at 15° 100 parts of

Alcohol, sp. gr. 0·800,	dissolve 0·591 of anthracene
" " 0·825,	" 0·574 "
" " 0·830,	" 0·491 "
" " 0·835,	" 0·475 "
" " 0·840,	" 0·460 "
" " 0·850,	" 0·423 "
Ether . . .	" 1·175 "
Chloroform . .	" 1·736 "
Carbon disulphide .	" 1·478 "
Glacial acetic acid .	" 0·444 "
Benzene . . .	" 1·668 "
Petroleum . . .	" 0·394 "

<sup>1</sup> Auerbach, *Das Anthracen*, 2nd ed., p. 12.

<sup>2</sup> *Dingl. polyt. J.*, cxcvi., p. 543.

<sup>3</sup> *Chem. News*, xxx., p. 204. His anthracene probably was not quite pure.

According to Bechi,<sup>1</sup> 100 parts of

Abs. alcohol at 16° dissolve 0.076 ; when boiling, 0.83 anthracene.

Toluene „ 16°.5 „ 0.92 ; at 100°, 12.94 „

Its solution in benzene, when exposed to sunlight, soon deposits crystals of *paranthracene* which resist the action of solvents and concentrated acids and fuse at 244°, being reconverted into anthracene. Ordinary sulphuric acid on gentle heating dissolves anthracene and acquires a greenish colour; at a higher temperature sulphonic acids are formed. Fuming sulphuric acid acts violently upon it. Oxidizing agents convert it into anthraquinone; reducing agents into hydrocarbons richer in hydrogen; nitric acid into nitro-compounds. Dissolved in benzene, together with picric acid, it yields ruby-coloured crystals, fusing at 170° and decomposed by alcohol. With dinitroanthraquinone (Fritzsche's reagent) it gives shining, rhomboidal, purple plates: if it is not quite pure, the plates are blue; if too impure, the reaction fails altogether.<sup>2</sup> By the action of light it passes over into dianthracene, but this reaction is reversed by keeping the product in the dark (Luther and Weigert, *Chem. Zentr.*, 1904, ii, p. 117; 1905, i., p. 1152).

Its molecular heat of combustion at constant pressure is = 1694.3 cal. (Stohmann, Kleber, and Langbein, *J. prakt. Chem.*, xl, pp. 128 and 202).

### *Hydrides of Anthracene.*

E. Lehmann (Inaug. Diss., München, 1911) has found hydrides of anthracene and phenanthrene in the liquid portion of anthracene oil, but was not able to prepare any of them in the pure state.

### *Anthracene dihydride, C<sub>14</sub>H<sub>12</sub>*

Prepared by Graebe and Liebermann;<sup>3</sup> occurs in coal-tar, crystallizes in colourless plates, similar to naphthalene; fuses at 106°, begins to sublime at the same temperature, and distils at 305° without decomposition. It volatilizes with aqueous or

<sup>1</sup> *Ber.*, 1879, p. 1978.

<sup>2</sup> Fritzsche, *Z. für Chemie* [2], iii., p. 289.

<sup>3</sup> *Ber.*, 1868, p. 187.

alcoholic vapours. It has a peculiar smell, especially at a higher temperature. It is insoluble in water, easily soluble in alcohol, ether, and benzene. In the solid state it shows no fluorescence; but its solutions have a blue fluorescence. It does not, like anthracene, yield a compound with picric acid.

*Anthracene hexahydride, C<sub>14</sub>H<sub>10</sub>.*

occurs together with the preceding; fuses at 63°, and boils at 290°; its physical properties, solubilities, etc., are quite similar to those of the dihydride. A tetrahydride, which was formerly assumed, does not exist.

*Anthracene perhydride, C<sub>14</sub>H<sub>24</sub>.*

Obtained by Lucas (*Ber.*, 1888, p. 2511) by reducing anthracene with red phosphorus and hydriodic acid at 250°. Colourless scales, melting at 88°, boiling at 270°.

*Paranthracene, C<sub>28</sub>H<sub>20</sub>.*

does not occur as such in coal-tar, but is formed by the action of sunlight on solutions of anthracene, from two molecules of C<sub>14</sub>H<sub>10</sub> (Elbs<sup>1</sup> and Orndorf and Cameron<sup>2</sup>). It melts at 272° to 274°, and is thereby reconverted into anthracene.

*Monomethylantracene, C<sub>15</sub>H<sub>12</sub> = C<sub>14</sub>H<sub>9</sub> · CH<sub>3</sub>.*

Discovered in 1874 by Weiler,<sup>3</sup> and since then often examined; occurs in coal-tar in small quantities.<sup>4</sup> It has been synthetically produced by Kraemer and Spilker, by overheating the vapours from *m*-xylene-styrolene.<sup>5</sup> It crystallizes from hot alcohol in thin, very bright, light yellow scales; fuses at 200° (Weiler, Fischer) or 208° to 210° (Wachendorff and Zincke); sublimes in greenish scales; boils above 360°. Insoluble in water; little soluble in alcohol, ether, and glacial acetic acid; easily soluble in chloroform, carbon disulphide, and benzene. Nitric and sulphuric acids dissolve it slowly cold, more quickly when hot.

<sup>1</sup> *J. prakt. Chem.*, xlv., p. 467.

<sup>2</sup> *Amer. Chem. J.*, xvii., p. 658.

<sup>3</sup> *Ber.*, 1874, p. 1185.

<sup>4</sup> Japp & Schultz, *ibid.*, 1877, p. 1049.

<sup>5</sup> *Annalen*, clxix., p. 207.

With picric acid it yields a compound similar to that obtained from anthracene. The formula given by Laurent for his "paranaphthene" was also  $C_{15}H_{12}$ ; but he could not have had a pure compound before him.

*Isomethylantracene,  $C_{15}H_{12}$ ,*

has been found by Börnstein (*Ber.*, 1906, p. 1238) in a tar obtained from a non-bituminous Westphalian coal, when distilled at the low temperature of  $500^{\circ}$  C. It melts at  $202^{\circ}$  to  $204^{\circ}$ , can be sublimed when cautiously heated, yields a red picrate, and dissolves with violet-blue fluorescence in the ordinary organic solvents.

Gross (*J. prakt. Chem.*, 1910, lxxxii, p. 231) obtained it as a by-product in the preparation of tritolyl-methane from formaldehyde and toluene.

*Dimethylantracene,  $C_{16}H_{14}$ ,*

was synthetically prepared by Van Dorp in 1872,<sup>1</sup> but not directly proved to exist in coal-tar. This is, however, made most probable by Kraemer and Spilker's synthesis from pseudocumenestyrolene, like its preceding homologue. It resembles the preceding, and fuses at  $224^{\circ}$  to  $225^{\circ}$ .

Lavaux (*Comptes rend.*, 1904, p. 44) obtained by the action of methylene chloride on toluene in the presence of aluminium three different methylantracenes, fusing at  $240^{\circ}$ ,  $244^{\circ}$ , and  $86^{\circ}$  respectively.

The methylated anthracenes cause the alizarin prepared from such material to assume a yellow tint, and thus to lose in quality.

*Phenanthrene,  $C_{14}H_{10}$*

This isomer of anthracene was discovered simultaneously by Graebe<sup>2</sup> and by Fittig and Ostermeyer.<sup>3</sup> It is found in the last fraction of the coal-tar oils, as a constant companion of anthracene, and forms a large portion of the crude anthracene. It is obtained from the raw material by a long series of crystallizations from alcohol, in which it is much more soluble

<sup>1</sup> *Berl. Ber.*, 1890, pp. 3169 and 3269.

<sup>2</sup> *Ber.*, 1873, p. 861.

<sup>3</sup> *Annalen*, cxlvi., p. 361.

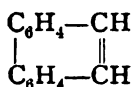
than anthracene, and is also obtained in the factories in the purification of the latter; most easily from crude anthraquinone by extracting it with alcohol and recrystallization. It is best to remove phenols and acridine by treating the product with caustic-soda solution and sulphuric acid. Moreover, its lower boiling-point can be utilized for a preliminary separation of it from anthracene; its much lower fusing-point facilitates its identification.

Phenanthrene, when pure, crystallizes from alcohol in colourless scales with a faint blue fluorescence. According to former statements, it fuses at  $99^{\circ}$  to  $100^{\circ}$ , and boils at about  $320^{\circ}$  to  $322^{\circ}$  (Kraemer). Weger (*Z. angew. Chem.*, 1909, p. 342) however states the fusing-point =  $96^{\circ}$ , the boiling-point =  $340^{\circ}$  (corr.). It sublimes in scales less easily than anthracene. It dissolves at  $13^{\circ}\cdot5$  in 48 or 50 parts of alcohol (readily when hot); also in ether, benzene, glacial acetic acid, and carbon disulphide. In alcoholic solution it yields with picric acid reddish-yellow needles, fusing at  $143^{\circ}$  to  $145^{\circ}$  and soluble in hot alcohol without decomposition. Nitric acid dissolves it, forming a nitro-compound; sulphuric acid at  $100^{\circ}$  forms a sulphonic acid. Bechi (*loc. cit.*) gives its solubility as follows:—In 100 parts of

Absolute alcohol, at  $16^{\circ}$  = 2.62, at  $78^{\circ}$  = 10.8 parts.

Toluene, „  $13^{\circ}\cdot5$  = 33.02, „  $100^{\circ}$  in all proportions.

The structural formula of phenanthrene is now generally assumed to be



*i.e.*, it is a derivative of diphenyl. This is absolutely proved by the synthesis from benzene and cumarone (Kraemer and Spilker), and from  $\alpha$ -phenylorthodiazocinnamic acid (Pschorr).<sup>1</sup> Its formation from naphthalene has been studied by Rabe;<sup>2</sup> Jackson and White<sup>3</sup> obtained it from ortho-brominated benzyl-bromide.

Graebe (*Ber.*, 1904, p. 4145) has shown that it is formed by the action of strong heat on ethyl and methylfluorene, the penta-nucleus thus passing over into the hexa-nucleus, with

<sup>1</sup> *Ber.*, 1896, p. 496.

<sup>2</sup> *Ibid.*, 1898, p. 1896.

<sup>3</sup> *Jahresh. d. Chem.*, 1880, p. 462, and 1882, p. 732.



loss of hydrogen. A. Werner, with some of his students, has made very valuable additions to the chemistry of phenanthrene (*Annalen*, cccxxi. and cccxxii.; *Chem. Zentr.*, 1902, ii., 56, 281), and so have Pschorr and his students (*Ber.*, xxxv., p. 2726; *Chem. Zentr.*, 1902, ii., 642).

It was formerly regarded as a worthless substance, only used for the manufacture of soot, but it seems now to take its rank among the valuable constituents of crude anthracene. It has been employed for the preparation of colouring matters, and its close relations to the opium alkaloids (morphine, codein, thebain) give the prospect of its employment for their synthetical preparation. It is obtained from crude anthracene, or preferably from the so-called "anthracene residues," from which it is got by extracting them with benzol hydrocarbons, and is thus separated from the anthracene still present and from carbazol. About 3 per cent. of the latter, then, still remain in the crude phenanthrene; this impurity is removed by alkaline fusion in the shape of potassium carbazolate. Even by repeated solutions, it is not possible to remove all the anthracene, but this can be achieved in other ways, ultimately obtaining a product containing less than 0.5 per cent. anthracene (Weger).

The *hydrides of phenanthrene* have been synthetically prepared, but not yet found in coal-tar (Graebe, Liebermann, and Spiegel, Bamberger, Lodter, and Bretan). The same holds good of the *methylphenanthrene*, prepared by Graebe.

*Pseudophenanthrene*,  $C_{16}H_{12}$ ,

fuses at  $115^{\circ}$ ; discovered by Zeidler<sup>1</sup> in that portion of crude anthracene which is soluble in acetic ether, together with

*Synanthrene*,  $C_{14}H_{10}$ ,

fusing at  $189^{\circ}$  to  $195^{\circ}$ . Nothing accurate is known of these bodies. Synanthrene is probably identical with methylanthracene.

*Fluoranthene*,  $C_{15}H_{10}$ .

*Syn. idryl.* Discovered in 1877 in coal-tar by Fittig and Gebhardt.<sup>2</sup> It probably stands in the same relation to fluorene

<sup>1</sup> *Chem. Centr.*, 1877, p. 566.

<sup>2</sup> *Ber.*, 1878, p. 241; *Annalen*, xcxi., p. 295.

( $C_{13}H_{10}$ ) as phenanthrene ( $C_{14}H_{10}$ ) to diphenyl ( $C_{12}H_{10}$ ). It accompanies pyrene in the highest-boiling fractions of coal-tar, and can be separated from pyrene only by many crystallizations from alcohol, preferably those of its compound with picric acid. It crystallizes from dilute alcohol in broad, shining, large plates; from a concentrated solution, in needles. It fuses at  $109^{\circ}$ , and afterwards sublimes; it boils in a partial vacuum (at a pressure of 60 mm.) at  $250^{\circ}$ . It dissolves with difficulty in cold alcohol, readily in ether, chloroform, benzene, carbon disulphide, glacial acetic acid, and boiling alcohol; when dissolved in concentrated sulphuric acid by gently heating, it gives it a greenish-blue, at a higher temperature a blue, and ultimately a brown colour. With nitric acid it yields a trinitro-product; with picric acid in alcoholic solution, reddish-yellow needles fusing at  $183^{\circ}$ , and decomposed on boiling with water or addition of ammonia.

Goldschmidt (*Monatsh.*, i., p. 225) prepared hydrofluoranthrenes,  $C_{15}H_{12}$  and  $C_{15}H_{18}$ .

*Pyrene,  $C_{16}H_{10}$*

Laurent, in 1837, found pyrene in coal-tar, but probably obtained it only in a very impure state. Graebe, in 1870, prepared it in the pure state.<sup>1</sup> The fractions boiling above anthracene (that is, distillates from tar-pitch) are extracted with carbon disulphide, the filtrate is evaporated to dryness, the residue dissolved in alcohol, and a precipitate is produced by an alcoholic solution of picric acid, which is several times recrystallized from alcohol, and then decomposed by ammonia. The separated pyrene is recrystallized from alcohol. Colourless tables, fusing at  $148^{\circ}$ , subliming with difficulty, and boiling considerably above  $360^{\circ}$ . Little soluble in cold alcohol, easily in carbon disulphide, ether, benzene, and hot alcohol. Bechi (*loc. cit.*) states its solubility in 100 parts of

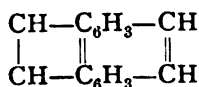
Absolute alcohol, at  $16^{\circ}$  = 1.27, at  $78^{\circ}$  = 3.08 parts.

Toluene,            ,,  $18^{\circ}$  = 16.54,   ,,  $100^{\circ}$  very great.

It yields a nitro-product. Its picrate forms long red needles fusing at  $222^{\circ}$ , decomposed slowly by boiling water, at once by alkalis. Graebe regards it as phenylene-naphthalene,

<sup>1</sup> *Annalen*, clviii., p. 285.

$C_{10}H_6(C_6H_4)$ ; it may also be represented as a diphenyl derivative in which the two nuclei are once more connected by two  $C_2H_2$  groups.



*Cf.* also Bamberger and Philip (*Annalen*, ccxl., p. 147).

*Chrysene*,  $C_{18}H_{12}$

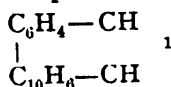
Discovered in 1817 by Robiquet and Colin when distilling amber, in 1837 by Laurent in coal-tar; afterwards investigated by many chemists. Chrysene is obtained in larger quantity only by distilling pitch down to coke, mixed with pyrene as a yellow tough mass, sometimes as a dry powder. On extracting this mass with carbon disulphide, chrysene remains behind, and is recrystallized from hot glacial acetic acid or heavy tar-oil. The latter and oil of turpentine are its best solvents; carbon disulphide in the cold dissolves only traces. Bechi states its solubility in 100 parts of

Absolute alcohol, at  $16^\circ = 0.097$ , at  $78^\circ = 0.17$  part.

Toluene,                   ,,  $18^\circ = 0.24$ ,   ,,  $100^\circ = 5.39$  parts.

Spilker (*Ber.*, xxvi., p. 1454) prepared it by overheating the vapours of indene; Klotz (*ibid.*, xxiii., p. 84) by overheating the vapours of certain high-boiling fractions of heavy benzol in red-hot tubes.

Chrysene usually forms loose, shining, yellow scales (rhombohedral with straight end-face), whose colour, however, is caused by a tenaciously adhering mixture of another substance (chrysogen); in a perfectly pure state it is white. It fuses at  $250^\circ$ , sublimes similarly to anthracene, boils at  $436^\circ$ , but is at the same time partly decomposed. With picric acid and binitro-anthraquinone it forms compounds. In concentrated sulphuric acid it dissolves on being heated, with a purple colour; nitric acid yields nitro-products. It is a member of the series, increasing by  $C_4H_2$ , to which benzene, naphthalene, phenanthrene, chrysene, and picene belong; probably it is



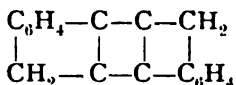
<sup>1</sup> Graebe and Bungener, *Ber.*, 1879, p. 1078; Bamberger and Kranzfeld, *ibid.*, 1885, p. 1931.

The accuracy of this formula has been proved by the syntheses of Kraemer and Spilker (*supra*), and of Bamberger and Chattaway (*Ber.*, 1893, p. 1745).

The *hydrides of chrysene*, investigated by Liebermann and Spiegel<sup>1</sup> probably occur also in coal-tar. They prepared the chrysene hydride  $C_{18}H_{28}$  (an oil boiling at  $360^\circ$ ), and chrysene perhydride,  $C_{18}H_{30}$ , white needles, fusing at  $115^\circ$ , boiling at  $353^\circ$ .

*Truxene*,  $C_{18}H_{12}$ .

This hydrocarbon, which has been prepared from hydrindene, from dichlorindene, from hydrocinnamic acid, etc., by various chemists (Hausmann, *Ber.*, xxii., 2022; Liebermann and Bergami, *ibid.*, xxii., 786; by Kipping, *ibid.*, xxvi. [2], 607; *Proc. Chem. Soc.*, Nos. 112 and 117; *J. Chem. Soc.*, lxxv, pp. 276 and 495; Monthey, *Ber.*, xxxii., p. 2476) has been found in coal-tar pitch by Weger and Billmann (*Ber.*, xxxvi., 1903, p. 540). Kraemer (*ibid.*, p. 645) considers it an important constituent of the pitch. Formula :



It appears in yellow or orange-red needles, melting at  $365^\circ$  to  $368^\circ$  (Liebermann, *Ber.*, xxvii., p. 2417). In the purest state (obtained by distillation) it is colourless. Not soluble in all ordinary solvents; but a little in boiling xylene, chloroform, aniline, and nitrobenzene. Is but slowly acted upon by fusing potash, more so by prolonged boiling with strongest nitric acid, nitrophthalic acid and other products being formed. Treatment with the chromic acid mixture produces tribenzoylene-benzol.

*Chrysogen*.

Discovered in 1862 by Fritzsche<sup>2</sup> in coal-tar. It is the substance whose intense orange colour, even in the smallest quantity, imparts its tint to other bodies, *e.g.*, to chrysene. Its formula is not yet established; it contains above 94 C per cent. It is isolated by repeated crystallization from light tar-oil and washing with ether and alcohol. It dissolves in 500 parts of boiling or 2500 parts of cold benzene, 2000 of boiling or 10,000

<sup>1</sup> *Ber.*, 1889, p. 135.

<sup>2</sup> *Z. für Chemie* [2], ii., p. 139.

of cold glacial acetic acid. It is best obtained by crystallization from boiling alcohol, in yellow scales, cohering like sal-ammoniac; the thinnest scales are pink, with gold-green lustre. Even  $\frac{1}{8000}$  of it imparts to naphthalene an intense yellow colour; but its solutions are quickly bleached in the sun, star-shaped groups of colourless needles being formed. It fuses at  $280^{\circ}$  to  $290^{\circ}$ , being partly decomposed; in concentrated sulphuric acid it dissolves without change.

*Retene*,  $C_{18}H_{18}$ .

Discovered in 1837 by Fikentscher and Tromsdorff, in coal-tar by Kraus,<sup>1</sup> studied especially by Fritzsche<sup>2</sup> and by Bamberger and Hooker.<sup>3</sup> Shining, unctuous scales, devoid of smell and taste, fusing at  $98^{\circ}$  to  $99^{\circ}$ , solidifying again at  $90^{\circ}$  to  $95^{\circ}$ . boiling at  $350^{\circ}$  without change, but volatilizing a little even at the ordinary temperature, strongly in the water-bath. Sinks down in cold water, but floats in hot alcohol, ether, fatty and essential oils. At a red heat it yields much anthracene. It has been proved by Bamberger and Hooker to be methyl-isopropyl-phenanthrene. It is most easily prepared by distilling resin-oil with sulphur (priv. comm. from J. Kraemer). Its dodecahydride has been prepared by Liebermann and Spiegel (*supra*).

Several *hydrides of retene* ( $C_{18}H_{22}$ ,  $C_{18}H_{30}$ ,  $C_{18}H_{32}$ ) are also known.

*Succisterene*

is hardly a distinct chemical compound, but probably a mixture, Pelletier and Walter describe it as devoid of smell and taste, fusing at  $160^{\circ}$  to  $162^{\circ}$  and distilling above  $300^{\circ}$ , very little soluble in alcohol and ether. Analysis yielded 95.5 C and 5.6 H per cent.

*Picene (Parachrysene)*,  $C_{22}H_{14}$ .

Discovered by Burg<sup>4</sup> in brown-coal-tar, but very probably also present in the heaviest coal-tar oils; identical with Rasenack's parachrysene.<sup>5</sup> It is very similar to chrysene, but even less

<sup>1</sup> *Ann. Chem. Pharm.*, cvi., p. 391.

<sup>2</sup> *J. prakt. Chem.*, lxxv., p. 281.

<sup>3</sup> *Annalen*, ccxxix., p. 102.

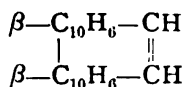
<sup>4</sup> *Ber.*, 1880, p. 1834.

<sup>5</sup> *Ibid.*, 1873, p. 1041; *Wagner's Jahresber.*, 1873, p. 813.

soluble, viz., very little in boiling glacial acetic acid, benzene, and chloroform, best in coal-tar oils; boiling between  $150^{\circ}$  and  $170^{\circ}$ . Its fusing-point is higher than that of any other known hydrocarbon, viz.,  $337^{\circ}$  to  $339^{\circ}$ , corrected =  $345^{\circ}$ , and it boils at  $518^{\circ}$  to  $520^{\circ}$ . It dissolves in concentrated sulphuric acid, with a green colour.

Precisely the same body was found by Graebe and Walter<sup>1</sup> in a product obtained by dry distillation of the purification residue of Californian petroleum. They found its formula =  $C_{22}H_{41}$ . It fuses at  $330^{\circ}$  to  $345^{\circ}$ , and boils (as determined by Crafts's air-thermometer) at  $518^{\circ}$  to  $520^{\circ}$ . Hence also its boiling-point exceeds that of any other hydrocarbon of known formula.

Bamberger and Chattaway<sup>2</sup> obtained it in a purer state and found its fusing-point  $364^{\circ}$ . They proved it to be  $\beta\beta$  dinaphthylene-ethylene—that is, the phenanthrene of the naphthalene series:



Lespicau<sup>3</sup> has prepared it synthetically by the action of ethylene bromide on naphthalene in the presence of aluminium. Hirn (*Berl. Ber.*, xxxii., p. 3341) states that it is formed by distilling  $\alpha$ -dinaphthostilbene through a red-hot tube.

The *hydrides of picene* have been prepared by Liebermann and Spiegel (*loc. cit.*), and found by Boyen (*Chem. Zeit.*, 1889, pp. 870 and 905) in the high-boiling oils from browncoal-tar.

#### *Benzerythrene*, $C_{24}H_{18}$ .

Discovered by Berthelot,<sup>4</sup> prepared in the pure state by Schultz,<sup>5</sup> and recognized as triphenylbenzene. Fuses at  $307^{\circ}$  to  $308^{\circ}$ . Small, white, shining, strongly electric scales. Little soluble in alcoholic or even boiling glacial acetic acid, more so in hot benzene; soluble in sulphuric acid, with a green colour.

<sup>1</sup> *Ber.*, 1881, p. 175.

<sup>2</sup> *Ibid.*, 1893, p. 1751; and *Liebig's Annalen*, cclxxxiv., p. 52.

<sup>3</sup> *Ibid.*, 1891, Ref. p. 963.

<sup>4</sup> *Ann. Chim. Phys.* [4], ix., p. 458.

<sup>5</sup> *Ber.*, 1878, p. 96.

*Crackene, C<sub>24</sub>H<sub>18</sub>.*

was first isolated from the "red-pitch" of the "cracking-boilers" used in distilling mineral oils, by Klaudy and Fink (*Monatsh.*, xxi., p. 118), and afterwards found in some coal-tars by Börnstein (*Ber.*, 1906, p. 1241; *cf.* also *Chem. Zentr.*, 1906, ii., p. 921). It fuses at 308° and sublimes when cautiously heated; over 500° C. it boils with decomposition. Very little soluble in alcohol, soluble in boiling benzene, cumene, petroleum-spirit, glacial acetic acid, chloroform, and acetone. Sulphuric acid dissolves it with dark blue colour. It is oxydized to a quinone by a solution of chromic acid in acetic acid.

*Bitumens.*

Badly characterized hydrocarbons, fusing with great difficulty, assumed to be present in coal-tar pitch. Carnelley<sup>1</sup> distinguishes two bitumens:—one boiling at 427° to 439°, which is readily soluble in benzene, and carbon disulphide, moderately in ether; and the other boiling above 439°, hardly soluble in benzene, but more easily in carbon disulphide. The latter softened at 190°, began to fuse at 220°, but was not quite liquid till it reached 330°. Both were black masses with conchoidal fracture. Evidently Carnelley himself does not assume that these two bodies were homogeneous compounds. (*Cf.* also, *supra* p. 261, what Kraemer says of truxene.)

## OXYGENIZED COMPOUNDS.

*Water, H<sub>2</sub>O.*

This is always contained in coal-tar, partly mechanically enclosed in the free state, partly in chemical combination with phenols and other substances.

Mallmann (*J. Gasbeleucht.*, 1905, p. 827) found in 188 specimens of gas-tar from 5 to 33 per cent. water, keeping in solution principally ammonia and ammonium salts, with small quantities of pyridine and other organic bases, phenols, etc. It is, of course, mechanically enclosed "ammoniacal liquor," and is worked up with this for ammonia.

<sup>1</sup> *J. Chem. Soc.*, 1880, p. 714.

*Methylic Alcohol*,  $\text{CH}_3\text{O}$ .

*Syn.* wood-spirit, wood-naphtha. Boils at  $63^\circ$ ; sp. gr. at  $0^\circ$  0.818, at  $20^\circ$  0.798. Occurs in wood-tar, and especially in crude wood-vinegar; not yet proved with certainty to occur in coal-tar, but found by Rosenthal (*Z. angew. Chem.*, 1901, p. 665) in lignite-tar.

*Ethylic Alcohol*,  $\text{C}_2\text{H}_5\text{O}$ .

*Syn.* spirit of wine. Boils at  $78^\circ.5$ ; sp. gr. at  $0^\circ$  0.8095, at  $15^\circ.5$  0.7939. According to Witt,<sup>1</sup> it constitutes 2 per cent. of crude benzol; Vincent and Delachanal<sup>2</sup> also confirm this statement; but Kraemer<sup>3</sup> questions the fact, as do also K. E. Schulze (*vide supra*) and Heusler (*Ber.*, 1895, p. 488). Possibly the mistake arose from the circumstance that the "crude benzol" of Witt and of Vincent had already been treated with sulphuric acid and caustic-soda liquor, in which case it might happen that, from the ethylene dissolved in the tar, sulphovinic acid would be formed, and decomposed by the alkaline treatment with formation of alcohol. Watson Smith also explains the formation of alcohol in this way; he could find only small traces of alcohol in London benzene.

*Acetic Acid*,  $\text{C}_2\text{H}_4\text{O}_2$ .

Boils at  $119^\circ$ ; sp. gr. at  $15^\circ$  1.057. Extremely important as is its occurrence in wood-tar, it seems to be nearly, if not quite absent from coal-tar. Vincent and Delachanal (*loc. cit.*) found it on distilling crude benzol with alkali, as a product of the decomposition of methylic cyanide. Rosenthal (*loc. cit.*) found this in lignite-tar, together with propionic acid, *n*-butyric acid, and *n*-valerianic acid.

*Acetone*,  $\text{C}_3\text{H}_6\text{O} = \text{CH}_3 - \text{CO} - \text{CH}_3$ .

Boils at  $56^\circ$ ; sp. gr. 0.7921 at  $18^\circ$ . Soluble in water, alcohol, ether, etc., in all proportions. Very inflammable. Heusler has obtained it from "first runnings" of benzol by treatment with water; Rosenthal (*loc. cit.*) from lignite-tar.

<sup>1</sup> *Chem. Centr.*, 1878, p. 415.      <sup>2</sup> *Comptes rend.*, lxxvi., p. 340.

<sup>3</sup> *Chem. Ind.*, 1878, p. 126.



*Methylethylketone*,  $C_4H_8O$ 

found, together with acetone, by K. E. Schulze (*Ber.*, 1887, p. 411) in first runnings from benzol after the treatment with sulphuric acid; he thinks it probable that both this and acetone had been formed by the action of sulphuric acid on methyl- and ethyl-acetylene. Rosenthal (*loc. cit.*) found it in lignite tar.

*Acetophenone (Phenylmethylketone)*,  $C_8H_8O$ 

was found by Weissgerber (*ibid.*, 1903, p. 753) in the heavy benzols of trade, together with small quantities of other aromatic ketones, not isolated. It seems as if the ketones, like phenols and bases, belonged to the regular constituents of coal-tar.

*Benzoic Acid*,  $C_7H_6O_2$ .

Melting-point  $121^{\circ}.4$ ; boils at  $249^{\circ}.2$ . Found in the residues from the manufacture of phenol by K. E. Schulze (*Ber.*, 1885, p. 615). It is perhaps not present as such in the tar, but is only formed from benzonitrile during the treatment for phenols (see below under "benzonitrile").

*Phenol (Carbolic Acid)*,  $C_6H_6O$ .

*Syn.* phenylic acid, phenylic alcohol. Discovered in 1834 by Runge,<sup>1</sup> more thoroughly examined by Laurent, and subsequently by many chemists. It was for a long time confused with Reichenbach's "Creosote" from beech-wood tar, in spite of Runge's and Laurent's protestations, on the authority of Reichenbach, Gmelin, and others: hence "creosote" came to be practically synonymous with "carbolic acid" (*acide phénique*), until all doubts were removed by Goupil-Besanez.<sup>2</sup>

The history, manufacture, application, and examination of carbolic acid are monographically treated by H. Köhler in his book: *Karbolsäure und Karbolsäurepräparate*, Berlin, 1891.

*Occurrence and Formation.*—Phenol is one of the most frequently occurring substances. It is found as such in nature; it is a product of the changes of substance, taking place in

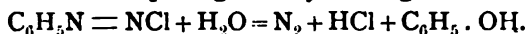
<sup>1</sup> *Poggend. Ann.*, xxi., p. 69; xxxii., p. 308.

<sup>2</sup> *Cf.* the History of Phenol, by Schorlemmer, *J. Soc. Chem. Ind.*, 1885, p. 152.

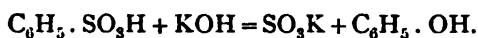
animal organisms, and is formed in many chemical processes, especially by the pyrogenetic decomposition of organic substances. Watson Smith (*loc. cit.*) found it in the products extracted from Japanese coal; Griffiths (*Chem. News*, xlix., p. 95) in many parts of the pine; Pebal and Freund (*Ann. Chem. Pharm.*, cxv., p. 19) in petroleum from Galicia; Markownikoff and Oglobin (*Chem. Zentr.*, xii., p. 607) in such from Caucasia; Wöhler (*Ann. Chem. Pharm.*, li., p. 46; lxvii., p. 360) in the "castoreum" secreted by beavers; Staedeler (*ibid.*, lxxvii., p. 18), Lieben (*ibid.*, supplement, vii., p. 240), Landolt (*Berl. Ber.*, iv., p. 770), Christiani (*Z. physik. Chem.*, ii., p. 273) in the urine of man and animals. Munk (*Berl. Ber.*, ix., p. 1596) found in normal human urine, secreted with mixed food, 0.004 g. phenol per litre; Salkowski (*ibid.*, ix., p. 1595; x., p. 842) in the same under pathological conditions up to 1.5575 g. Baumann (*ibid.*, ix., p. 54) found that phenol (and cresol) do not exist in urine as such, but in the form of a sulphuric ether. Brieger (*Z. physik. Chem.*, v., p. 366), Baumann (*ibid.*, i., p. 60; iii., p. 250), Weyl (*ibid.*, iii., p. 312) found it among the products of the putrefaction of albuminous substances, which, as proved by Baumann (*Berl. Ber.*, xii., p. 1450; xiii., p. 279), explains the occurrence of phenol in animal secretions.

Schultzen and Naunyn (*Arch. Anat. Physiol.*, 1867, p. 34) found that phenol is also formed directly from benzene in the animal organism. Hoppe-Seyler (*Berl. Ber.*, xii., p. 1551) obtained phenol from benzol by shaking with water and palladium hydride; Leeds (*ibid.*, xiv., p. 975) by the action of sunlight on phosphorus, covered with water and benzene. In both cases the oxidation of benzene into phenol is caused by the hydrogen peroxide formed. Friedel and Crafts (*Bull. Soc. Chim.*, xxxi., p. 463) found that phenol was also formed by passing oxygen through boiling benzene. These methods are chemically interesting, but their technical utilisation is not possible.

Large quantities of phenol are synthetically obtained by the oxidation of aniline by means of the method found by Peter Griess (*Ann. Chem. Pharm.*, cvi., p. 123, and many subsequent publications); converting the aniline into a diazo-compound and decomposing this by boiling with dilute acids:

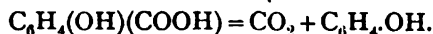


A most important way of preparing phenol was found at the same time and quite independently by Kekulé (*Z. f. Chem.*, N.F., iii., p. 193), Wurtz (*Comptes rend.*, lxiv., p. 749), and Dusart (*ibid.*, lxiv., p. 895), and has been specially studied by Degener (*J. prakt. Chem.*, N.F., xvii., p. 394), viz., the action of fusing potash on benzenesulphonic acid, the reaction being :



This synthesis of phenol has been technically utilized during periods of high prices of carbolic acid, and the phenol thus produced excelled by its remarkable purity and its mild odour ; but nowadays the phenol is produced from coal-tar in the same state of purity and at a cheaper price, so that its synthetical production has had to be almost entirely abandoned.

As shown by Graebe (*Ann. Chem. Pharm.*, cxxxiv., p. 143), Gerhard (*Ann. Chim. Phys.* [3], vii., p. 215), Rosenthal (*Z. f. Chem.*, 1869, p. 627), Klepl (*J. prakt. Chem.*, N.F., xviii., p. 159) phenol is quantitatively formed by heating the three isomeric benzoic acids, carbon dioxide being split off ;



Berthelot (*Comptes rend.*, lxviii., p. 539) observed the formation of phenol when passing the vapours of alcohol and acetic acid through a red-hot tube, and its production from acetylene by passing this gas into fuming sulphuric acid, and fusing the sulphonic acid thus formed with potash.

Phenol is also formed in a series of complicated chemical processes which cannot be enumerated in this place, and in the destructive distillation of many organic substances, such as wood (Marasse, *Ann. Chem. Pharm.*, cvii., p. 159), lignite (Rosenthal, *Chem. Zeit.*, 1890, p. 870), bones (Weidel and Ciamician, *Monatsh.*, i., p. 279). In coal-tar it is found in much greater proportion than in any other kind of tar.

*Properties of Phenol.*—In the absolutely pure state it forms long white needles, fusing at  $42^{\circ} \cdot 2$  into a clear, colourless liquid, and boiling (under a pressure of 760 mm.) at  $184^{\circ}$  without decomposition. Ordinary "pure" phenol, which contains traces of cresol or water, fuses at about  $35^{\circ}$  and boils at  $188^{\circ}$ . Hence the phenol examined by Adrieenz,<sup>1</sup> and considered exceptionally pure, which fused at  $37^{\circ} \cdot 8$ , solidified at  $34^{\circ} \cdot 3$ , and

<sup>1</sup> *Ber.*, 1873, p. 443.

boiled at  $183^{\circ}\cdot3$  to  $184^{\circ}\cdot1$ , was not absolutely pure. Really pure phenol, fusing at  $42^{\circ}$ , is less deliquescent than that melting at  $35^{\circ}$ , which contains a little cresol. In damp air phenol absorbs water, and its fusing-point is lowered by the formation of a *hydrate*,  $C_6H_5O, H_2O$ , containing 16.07 per cent. of water and fusing at  $17^{\circ}\cdot2$ .<sup>1</sup> It seems to be the same as that obtained by Calvert on exposing a mixture of 4 parts of phenol with 1 part of water to a temperature of  $4^{\circ}$ , although he states its fusing-point to be  $16^{\circ}$ , and its formula  $2(C_6H_5O), H_2O$ . The hydrate begins to lose water at  $100^{\circ}$ , and thus gradually arrives at the boiling-point of anhydrous phenol.

In very damp air the hydrate absorbs still more water and then remains liquid. If as much water is added to phenol as will combine with it, the resulting liquid contains about 27 per cent. water, almost exactly corresponding to the hydrate  $C_6H_5O, 2H_2O$ . But on shaking this liquid with 4 vols. of benzene, it gives up the whole of its phenol to the latter, the water being separated (Allen).

The specific gravity of phenol at  $18^{\circ}$  is 1.065; its expansion for the temperature  $t$  at the pressure of 760 mm. is stated by H. Kopp as follows :

$$V_t = 1 + 0.0006744t + 0.000001721t^2 - 0.0000000050408t^3.$$

Adrienz (*loc. cit.*) gives the following table of the volumes of phenol :—

Temperature.	Spec. grav.	Volume.
Degrees.		
40	1.05433	1.01504
50	1.04663	1.02259
60	1.03804	1.03036
70	1.02890	1.04028
80	1.01950	1.04984
90	1.01015	1.05951
100	1.00116	1.06899

In spite of being deliquescent, phenol is not very easily soluble in water, but is so in all proportions in alcohol, ether, benzene, glacial acetic acid, glycerin, etc. It is usually stated that phenol dissolves in 20 parts of water; and some give

<sup>1</sup> Allen, *Analyst*, iii., p. 319.

## 270 PROPERTIES OF COAL-TAR AND ITS CONSTITUENTS

even a much higher figure. Alexeieff gives the following data:—100 parts of water at 11° dissolve 4.83, at 35° 5.36, at 58° 7.33, at 77° 11.83 parts of phenol; at 84° both liquids mix in all proportions. On the other hand, 100 parts of phenol at 9° dissolve 23.3, at 32° 26.75, at 53° 31.99, at 71° 40.72 parts of water. But Allen states that liquid aqueous carbolic acid dissolves in 11.1 times its volume of cold water, corresponding to pure phenol dissolving in 10.7 times its weight of water, or to the aqueous solution containing 8.56 per cent.<sup>1</sup> According to Hamberg,<sup>2</sup> pure carbolic acid (fusing-point 40° to 41°, solidifying-point 39°, boiling-point 180° to 180°.5) dissolves at 16° or 17° in 15 parts of water, and at 40° in 2 vols. of liquor ammoniæ of sp. gr. 0.96 (forming a clear liquid which turns milky at 17° or 18°). Other statements, attributing to it a smaller solubility, may be explained by the presence of cresol, which lowers the solubility. The aqueous solution does not redden litmus; benzene, ether, carbon disulphide, or chloroform abstract phenol from its aqueous solution. Cold petroleum-spirit dissolves but little of it. Schweissinger (*Pharm. Zeit.*, 1885, p. 259) gives the following particulars respecting the solubility of phenol in petroleum-spirit. One part phenol requires for its solution:—

At	48°	42°	41°	39°	37°	35°	32°	29°	27°	25°
	1	2	3	4	5	6	7	8	9	10
	28°	21°	19°	16°						
	15	20	30	40	parts of petroleum-spirit.					

The solubility in paraffin oil is about the same. This property of phenol is utilized in the manufacture of loose crystals.

The smell of carbolic acid is very similar to that of wood-tar creosote (that is, smoky), but (like the taste) it is less pronounced in very pure phenol than in impure; so that in the former it can be masked by a few drops of geranium oil, which also render it permanently liquid. The taste of phenol is both hot and sweet; it acts violently upon the epidermis, turning it white and causing it to harden or shrink. Hence it must be

<sup>1</sup> Other observers have found that phenol containing some water is much more soluble in an excess of water than anhydrous phenol; this perhaps explains the difference between Allen's observations and those of other chemists.

<sup>2</sup> *Ber.*, 1871, p. 751.

cautiously handled; rubbing with a fatty oil lessens the pain and the bad effects of external contact with it. Internally it acts of course as a poison, both on account of its corrosive action on the epithelium and its property of coagulating albumen; it appears to act on the nervous system by paralyzing the nerve-centres. According to Allen, even a momentary contact of strong acid with an extensive surface of the lower parts of the body is mostly fatal, but it has comparatively little effect on the arms.

The poisonous and coagulating properties of phenol are clearly shown by its preventing the development of lower organisms, which renders it one of the most important agents for the prevention of fermentation and putrefaction, for Lister's treatment of wounds, etc.; and its technical application, apart from its employment in the manufacture of a few colouring-matters, of salicylic acid, etc., is exclusively based on its antiseptic property.

*Cf.* about the poisonous action of carbolic acid, Bokorny, *Chem. Zeit.*, 1906, p. 554.

The solutions of phenol in oil do not possess the same disinfecting power as those in water (Koch, Wolffhügel, and Knorre, *J. Soc. Chem. Ind.*, 1882, p. 244).

Phenol, if not quite pure, turns red more or less quickly, especially under the influence of air and light. The cause of this is not accurately known; perhaps it is owing to the formation of rosolic acid due to traces of mineral acids, in the presence of homologues and of oxygen. Frequently the reddening of phenol is attributed to traces of copper<sup>1</sup> or of other metals,<sup>2</sup> which are said to form compounds of a red colour with phenol, but not rosolic acid (Kremel<sup>3</sup>). Rosolic acid is assumed to be the cause by Yvon;<sup>3</sup> other oxidized compounds by Ebell.<sup>4</sup> *Cf.* also Richardson,<sup>5</sup> Bach,<sup>6</sup> Gordon, Boes, Reuter. Some ascribe the red coloration, not to impurities, but to the oxidation of phenol itself. According to Kraemer and Spilker,<sup>7</sup> the coloration is due to the influence of indene.

<sup>1</sup> *E.g.*, Sicha, *J. Soc. Chem. Ind.*, 1882, p. 397.

<sup>2</sup> Kremel, *Chem. Zeit.*, 1886, Rep. 14; Meyke, *Fischer's Jahresber.*, 1883, p. 513.

<sup>3</sup> *Pharm. J. Trans.*, 1881, p. 1051.

<sup>4</sup> *Repert. anal. Chem.*, 1884, p. 17.

<sup>5</sup> *J. Soc. Chem. Ind.*, xii., p. 414.

<sup>6</sup> *Monit. Scient.* [4], viii., p. 508.

<sup>7</sup> *Berl. Ber.*, 1890, p. 648.

The following reactions are characteristic for phenol:—A drop of a dilute solution of phenol gives with a solution of 1 part of molybdic acid in 10 of concentrated sulphuric acid a yellow-brown colour, soon turning purple. Heating to not above  $50^{\circ}$  assists the reaction. Since many other bodies cause the reduction of molybdic acid, this reaction is interfered with by them. By addition of ferric chloride (not in excess!) 1 part of phenol in 1000 or at most 1500 (not 3000, as usually stated) of water can be recognized by a purple colour; but some neutral salts interfere with this, and, on the other hand, other compounds show the same reaction. In the presence of much alcohol this reaction ceases altogether (Peters, *Z. angew. Chem.*, 1898, p. 1078). Raschig (*Z. angew. Chem.*, 1907, p. 2065) attributes this reaction to the formation of a ferri-salt of phenol, similar to the ferri-salicylate characterized by Hantzsch and Desch in 1902 (*Annalen*, cccxxiii., p. 1). Twenty c.c. of a solution of 1 part of phenol in 10,000 water, mixed with a very little liquor ammoniæ and then with a little freshly saturated chlorine-water, or, preferably, bromine-water, produce a deep indigo-blue colour. This reaction is very stable, the colour remaining unchanged for days and weeks even in the open air. Salkowski (*Z. anal. Chem.*, 1872, p. 94) gives special rules for this reaction. On heating phenol solutions with  $\frac{1}{3}$  to  $\frac{1}{2}$  their bulk of a 10- or 15 per cent. solution of mercurous nitrate, a pink colour appears, which is strongest one or two hours afterwards. This reaction is almost as sensitive as the next, and remains for some time. Landolt showed in 1871 that 1 part of phenol in 80,000 water can be discovered by means of fresh bromine-water, a white crystalline precipitate of tribromphenol ( $C_6H_3Br_3O$ ) being formed, but in the case of very dilute solutions not till some time has elapsed. Uranium acetate is recommended as a test for phenols by Orlow (*Chem. Zeit. Rep.*, 1902, p. 164). According to Fiora (*Chem. Centr.*, 1901, i., p. 843) pure phenol, when treated with peppermint oil, after some time, gives a greenish-blue coloration which disappears on heating, but reappears on cooling again. Cresols, etc., do not give this reaction.

Liebermann (*Berl. Ber.*, vii., p. 248) indicates the following reaction of all phenols. When adding them to sulphuric acid containing nitric acid, the mixture turns first brown, then green and blue, and yields a splendidly blue solution in alkalis.

Waller (*Chem. News*, xliii., p. 150) quotes many reactions of phenols, especially those different from wood-tar creosote.

Schaer (*Arch. Pharm.*, April 1881) also compares the various reactions of phenol.

Herzog (*Pharm. Zeit.*, 1907, p. 578) recommends as a reagent for phenols, diphenyl-urea-chloride, and upholds this against objections made by Raschig (*Pharm. Zeit.*, 1908).

The quantitative estimation of phenol will be described in Chapter IX., where also the commercial qualitative tests for "pure carbolic acid" will be given.

Phenol is the type of a whole class of bodies which stands, as it were, midway between alcohols and acids. Hence the older and industrially most usual name, "carbolic acid," is scarcely used in scientific language. The phenols form a class by themselves, viz., those aromatic compounds in which the hydrogen atoms of benzene nuclei are replaced by hydroxyl (OH). The hydrogen of the latter is easily replaced by metals or alcoholic radicals; but the other characteristics of a real acid are absent.

Phenol has a certain affinity to bases, as manifested by their use in extracting it from tar oils, but its acid properties are only about  $\frac{1}{1000}$  of those of carbonic acid (Walker, *Z. physik. Chem.*, xxxii., p. 137). Nevertheless, when brought into contact with potassium or sodium carbonate, it replaces half of the  $\text{CO}_2$ , with formation of bicarbonates, as described by Gentsch in 1903 in a number of patents, to which we shall refer in Chapter IX.

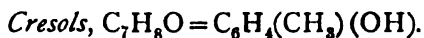
Phenol is consequently more soluble even in dilute alkaline solutions than in water, with formation of easily soluble and crystallizable compounds, (e.g., with potash, soda, or ammonia) called carbolates or phenates ( $\text{C}_6\text{H}_5\text{O}, \text{ONa}$ , etc.). These compounds are not very stable, but they are not decomposed by dilution with water. Ether and alcohol dissolve these compounds. Hence the phenols can be separated from the indifferent tar-oils by treatment with an alkali.

Concentrated sulphuric acid also dissolves phenol with formation of sulphonic acids, and thus removes it from tar-oils, which, however, easily retain a little of the sulphonic acid. Nitric acid yields nitro-products, one of which is technically important, viz., picric acid,  $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$ . In the presence of bodies which furnish methane-carbon, together with free mineral



acids and oxygen, rosolic acid,  $C_{19}H_{14}O_8$ , is formed. Upon this is based the technical preparation of coralline from phenol, oxalic acid, and sulphuric acid—and perhaps also the reddening of impure phenol, cresol [ $C_6H_4(CH_3)(OH)$ ] providing the methane-carbon. According to Kraemer (priv. comm.) the reddening of phenol is caused by the benzoic acid contained in crude phenol, which passes over on distillation, taking up a little iron from the still and forming therewith ferrous benzoate; this on exposure to the air is transformed into red ferric benzoate.

Döbner (*Ber.*, 1891, p. 1753) made the interesting observation that phenol in alkaline solution is split by potassium permanganate at a low temperature into inactive tartaric acid and oxalic acid.



*Syn.* oxytoluene, cresylic acid.

There are three isomers of this formula; coal-tar contains a mixture of all of these.

*Orthocresol* (1, 2) fuses at  $30^\circ$  and boils at  $191^\circ$  corr. (Weger); water dissolves at ordinary temperatures 2.5 vols. per cent. according to Gruber (*Z. angew. Chem.*, 1893, p. 613).

*Paracresol* (1, 4) forms colourless prisms, fusing at  $36.5^\circ$  and boiling at  $202^\circ$  corr. (Weger). It smells like phenol, and is little soluble in water (1.8 per cent. by volume). Its aqueous solution, like that of metacresol, is coloured blue by ferric chloride.

*Metacresol* (1, 3) boils at  $203^\circ$  (Weger); it is usually obtained as a thick liquid, not solidifying at  $-80^\circ$ ; but Staedel<sup>1</sup> has shown that it can be obtained solid on cooling down to  $-18^\circ$  and starting the crystallization by adding a crystal of phenol. The crystals melt at  $4^\circ$  (Weger). Water dissolves only 0.53 vol. per cent. (Gruber). It is asserted that metacresol is both the most efficient bactericide and yet the least poisonous of the phenols (Russig).

Formerly the cresols were only employed for disinfecting purposes, but nowadays they play an important part in the manufacture of coal-tar dyes, and are therefore separated from coal-tar in a pure form. Methods for separating the three cresols for analytical and technical purposes will be given in Chapter IX.

<sup>1</sup> *Ber.*, 1885, p. 3443.

Commercial cresylic acid (technically sometimes styled "tricrosol") is a mixture of the isomers which, according to K. E. Schulze (*Ber.*, 1887, p. 410), contains 40 per cent. meta-cresol, 35 orthocresol, 25 paracresol. Raschig (*Z. angew. Chem.*, 1900, p. 759) found on an average; 40 per cent. orthocresol, 35 per cent. metacresol, 25 per cent. paracresol. Creosote from lignite-tar, according to Boyen, *Berl. Ber.*, 1893, Ref. p. 151, contains 70 per cent. metacresol, 20 to 30 paracresol, and little or no orthocresol.

Gray (*J. Soc. Chem. Ind.*, 1902, p. 875) found in Scottish shale oils: 5 to 6 per cent. phenol, 12 to 15 per cent. *o*-cresol, 30 to 35 per cent. *m*-cresol, 30 to 35 per cent. xyenols, and a little guaiacol; *p*-cresol and creosol seem to be absent.

Commercial coal-tar cresol is a colourless, refractive liquid which does not solidify at  $-80^{\circ}$ . It has a specific gravity of 1.044, is much less soluble in water and alkalis, and boils at a higher temperature than carbolic acid, about  $185^{\circ}$  to  $203^{\circ}$ . It gives the same reaction with ferric chloride as carbolic acid, and is even more strongly acted upon by strong sulphuric and nitric acids. With bromine it gives a tribromo-compound,  $C_6HBr_3(CH_3)(OH)$ , liquid at ordinary temperatures. Its anti-septic properties are even more strongly marked than those of carbolic acid.

Allen gives the following table, showing the differences between carbolic acid (Calvert's No. 1) and cresylic acid (prepared from Calvert's No. 5 by fractionating):—

	Carbolic Acid.	Cresylic Acid.
1. Melting-point . . .	Solid at ordinary temperature; liquefied by addition of water; both absolute and hydrated acid are solidified by freezing-mixtures.	Liquid at ordinary temperature; neither absolute nor hydrated acid is solidified by freezing-mixture.
2. Boiling-point . . .	$182^{\circ}$ . . . . .	$198^{\circ}$ to $203^{\circ}$ .
3. Solubility of hydrated acid in cold water.	1 vol. in 11 . . . .	1 vol. in 29.
4. Solubility in strong solution of ammonia (sp. gr. 0.880).	Completely and readily soluble in equal volume; solution not precipitated by addition of less than $1\frac{1}{2}$ volume of water.	Almost insoluble; requires 16 volumes; then forms crystalline scales.

	Carbolic Acid.	Cresylic Acid.
5. Reaction with solution of caustic soda (free from alumina) containing 6 per cent. NaOH.	Completely soluble in equal volume. Addition of the alkali solution, even up to 6 volumes, causes no change.	Insoluble in small proportions. With large excess it disappears and forms crystalline scales.
6. Reaction with solution of caustic soda containing 9 per cent. NaOH.	Completely and readily soluble in equal volume. On addition of any proportion of water up to 7 volumes the liquid remains clear, but is precipitated by 8 measures of water. Soluble in 2 measures of soda, and not precipitated by less excess than 5 or 6 measures.	Soluble in equal volume, but precipitated by adding a few drops of water, the original volume separating when water is added amounting to 1 measure. The solution in soda is re-precipitated when the alkali solution is added to the extent of $3\frac{1}{2}$ measures.
7. Reaction with petroleum-spirit.	Absolute acid is miscible with hot petroleum-spirit in all proportions. Miscible with only $\frac{1}{2}$ vol. of cold petroleum-spirit, precipitated by greater proportion. With 3 vols. of petroleum-spirit, bulk unchanged; upper layer contains carbolic acid, which crystallizes out on sudden cooling by freezing-mixture.	Absolute acid miscible in all proportions. No separation of crystals or liquid produced by suddenly cooling solutions in 3 measures of petroleum-spirit.
8. Behaviour with glycerin of sp. gr. 1.258.	Miscible in all proportions. One measure of carbolic acid with an equal amount of glycerin is not precipitated on addition of 3 measures of water. In presence of cresylic acid less dilution is possible, 2 vols. of water being the maximum for a sample containing 25 per cent. cresylic acid.	Miscible in all proportions. One measure of cresylic acid, mixed with 1 measure of glycerin, is completely precipitated by 1 measure of water.

According to this table, cresylic acid is less soluble than carbolic acid in water, ammonia, glycerin, and caustic-soda liquor, but more easily in petroleum-spirit. Hence, though the presence of considerable quantities of cresylic acid can be discovered in carbolic acid, the utilization of the above reactions

for a quantitative estimation of these bodies is out of the question. An approximate estimation of this kind will be described later on. Water of the normal temperature dissolves 2.55 per cent. of the mixture of cresols in coal-tar (Gruber).

Lunge and Zschokke<sup>1</sup> have made experiments on the lowering of the fusing-points of pure phenol and pure paracresol by one substance being mixed with the other in definite proportions. The result of their observations are given in the following table:—

Phenol.	Paracresol.	Fusing-point.
Per cent.	Per cent.	Degrees.
100	0	+40.5
95	5	27.8
90	10	23.9
85	15	20.3
80	20	16.7
75	25	12.6
70	30	8.6
65	35	4.7
60	40	+0.75
55	45	-2.5
50	50	-2.5
45	55	-0.9
40	60	+1.2
35	65	3.5
30	70	6.7
25	75	12.4
20	80	16.2
15	85	20.8
10	90	25.9
5	95	28.5
0	100	+32.5

Since commercial cresylic acid also contains other isomers, the foregoing table cannot be directly utilized for analytical purposes.

The *pyrocresols*, first observed by Schwarz (*Ber.*, 1882, p. 2201), bodies of the formula  $C_{15}H_{14}O$ , have been proved by Zmerzlikar (*Z. angew. Chem.*, 1895, p. 468) to be secondary products formed in distilling crude phenol. Bott (*J. Soc. Chem. Ind.*, 1887, p. 846) has studied them in detail. They do not seem to be present in coal-tar.

<sup>1</sup> *Chem. Ind.*, 1885, p. 6.

*Xylenols (Xenols)*,  $C_8H_{10}O = C_6H_3(CH_3)_2OH$ .

Of the six xylenols admitted by theory, four are known. Some of these no doubt occur in coal-tar; it is also probable that the "*phlorol*" from the beechwood-tar (boiling at  $220^\circ$ ) is such a mixture. Marasse (*Ann. Chem. Pharm.*, clii., p. 75).

*Orthoxenol* (1, 2, 4) =  $C_6H_3(CH_3^1)(CH_3^2)(OH^4)$ . Fuses at  $65^\circ$  and boils at  $222^\circ$ . Crystallizes from water in long needles, from dilute alcohol in orthorhombic octahedra; yields a soluble sodium salt in thin needles.

*Orthoxenol* (1, 2, 3) fuses at  $73^\circ$  and boils at  $212^\circ$  to  $213^\circ$ .

*Metaxenol* I. (1, 2, 3) =  $C_6H_3(CH_3^1)(OH^2)(CH_3^3)$ . Long needles or plates, fuses at  $74.5^\circ$  and boils at  $211^\circ$  to  $212^\circ$  (Jacobsen), or at  $73^\circ$  and  $216^\circ$  respectively (Fittig and Hoogewerf).

*Metaxenol* II. (1, 3, 4) =  $C_6H_3(CH_3^1)(CH_3^3)(OH^4)$ . Colourless, strongly refractive liquid of sp. gr. 1.0362 at  $0^\circ$ ; does not easily solidify in the cold, except when brought into contact with a crystal of the same mass (Staedel and Hölitz, *Ber.*, 1885, p. 2921); the crystals melt at  $15^\circ$ . Boils at  $209^\circ$ , little soluble in water miscible with alcohol and ether. Its alcoholic solution is turned green by ferric chloride, its aqueous solution blue, whilst the other xenols do not give any reaction with that salt. Found in blast-furnace tar by Watson Smith (*J. Chem. Soc.*, Jan. 1866, and priv. comm.).

*Metaxenol* III. (1, 3, 5) fuses at  $63^\circ$  and boils at  $218^\circ$ .

*Paraxenol* (1, 3, 4) =  $C_6H_3(CH_3^1)(OH^3)(CH_3^4)$ . Colourless crystals, very like metaxenol I.; fuses at  $75^\circ$ , boils at  $208^\circ$  to  $209^\circ$ , sp. gr. at  $18^\circ = 0.9709$ . Solubility similar to that of the above.

There are higher phenols known, viz. :—*mesitylol*,  $C_9H_{11} \cdot OH$ , boiling at  $220^\circ$ ; *pseudocumenol*,  $C_9H_{11} \cdot OH$ , boiling at  $240^\circ$ ; *thymol*,  $C_{10}H_{13} \cdot OH$ , boiling at  $230^\circ$ ; *carvacrol* (same formula), boiling at  $233^\circ$  to  $235^\circ$ ; but their existence in coal-tar has not been proved.

*Dioxybenzenes (Oxyphenols).*—The oxyphenols have not been proved to occur in coal-tar, whilst in wood-tar they and their ethers are the most important constituents, especially *pyrocatechol*,  $C_6H_4(OH)_2$ , *homopyrocatechol*,  $C_6H_3(CH_3)(OH)_2$ , the methylic ether of the former (*guaiacol*) and that of the latter (*creosol*). Pyrocatechol has been found by Börnstein (*Berl. Ber.*, 1903, p. 4324) in the products of gasifying coal at a low temperature, by Gray (*loc. cit.*) in Scottish shale-oil. Spiegel (Ger. P. 68944 of the Gewerkschaft der Grube Messel) isolated it from the tar-water of the bituminous schist at Messel, Rosenthal (*Z. angew. Chem.*, 1903, p. 221) from the tar-water of the lignite of the Halle basin.



Both isomers have been found in the "green oils" obtained in the manufacture of anthracene by K. E. Schulze (*Annalen*, ccxxvii., p. 143).

*α Naphthol* forms brilliant needles, belonging to the monoclinic system, smells similar to phenol, and has a burning taste; sp. gr. 1.224. It melts at  $94^\circ$  to  $96^\circ$ , and boils at  $278^\circ$  to  $280^\circ$ . Sparingly soluble in hot water, easily in alcohol, ether, benzene, etc. Volatilizes with steam. A solution of chloride of lime with an aqueous solution of *α naphthol* causes a deep purple coloration and the separation of purple flakes; ferric chloride gives a white turbidity, soon passing into purple.

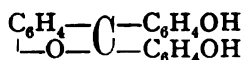
*β Naphthol* forms monoclinic scales, almost devoid of smell, of a burning taste; sp. gr. 1.217; melts at  $122^\circ$  to  $123^\circ$ , boils at  $294^\circ$ , volatilizes very little with steam. Solubility like that of *α naphthol*; but chloride of lime causes only a faint yellow coloration, and ferric chloride first a greenish colour, then the separation of permanently white flakes.



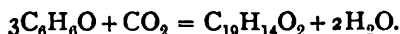
have been found, although not separated in the pure state, in the oils accompanying anthracene by Noelting (*Ber.*, 1884, p. 368) by treating the portion boiling above  $300^\circ$  with a solution of sodium hydrate.

*Rosolic Acid*,  $C_{19}H_{14}O_8$ .

*Syn. aurin.* Discovered in 1834 by Runge<sup>1</sup> in coal-tar; afterwards synthetically prepared simultaneously by Persoz<sup>2</sup> and by Kolbe and Schmitt,<sup>3</sup> but in a very impure state, by treating phenol with oxalic and sulphuric acids. Since then it has been examined by many prominent chemists; its constitution, and even its formula, was only definitely established in 1878, both by E. and O. Fischer and by Graebe and Caro. The generally recognized formula for rosolic acid from phenol, which is probably the same as that contained in tar, is  $C_{19}H_{14}O_8$ , or, structurally,



*i.e.*, a derivative of triphenylmethane, in which three hydrogen atoms are replaced by hydroxyl, and from which one molecule of water is abstracted.<sup>4</sup> Hence it is formed if three phenol remainders can attach themselves to a carbon atom of the fatty series (methane carbon); and it actually forms an inner anhydride of the trioxy-triphenylmethane-carbinol. It is often assumed that its formation from phenol, oxalic acid, and sulphuric acid is due to the liberation, from the oxalic acid, of  $CO_2$ , which in the nascent state gives up its oxygen to oxidize 4H of the phenols, and attaches the remainders to the vacant bonds of carbon, thus—



The accessory reactions which take place in the formation of corallin—*i.e.*, the crude product—cannot be noticed here. Nencki<sup>5</sup> and Watson Smith and Staub<sup>6</sup> attribute the formation of rosolic acid to the formic acid generated by the action of sulphuric acid upon phenol.

We have already (p. 271) pointed out that the conditions for the formation of rosolic acid are given when, besides phenol

<sup>1</sup> *Pogg. Ann.*, xxxi., pp. 65, 512; xxxii., pp. 308, 323.

<sup>2</sup> *Fr. P.* 54910, of 21st July 1861.

<sup>3</sup> *Ann. Chem. Pharm.*, cxix., pp. 119, 169.

<sup>4</sup> Graebe and Caro proposed to keep the name *aurin* for this compound, and to apply that of *rosolic acid* to the higher homologue, made from rosaniline; but this has not been generally accepted.

<sup>5</sup> *Ber.*, 1882, p. 1578.

<sup>6</sup> *J. Chem. Soc.*, 1884, p. 301.

itself, its higher homologues containing the methyl group  $\text{CH}_3$  are present, and if at the same time mineral acids can act upon it by separating water ; but there must also be an oxidizing action : thus—



Perhaps this explains why the reddening of phenol requires the presence of air, as well as the reddening of impure naphthalene, which in any case contains some unchanged phenol ; *cf.*, however, p. 271.

In any case it must be assumed that the rosolic acid found by Runge in coal-tar was only formed by acid treatment of the products. (It has not yet been proved whether a mineral acid is absolutely necessary or not.) He obtained it by exhausting the residues from the distillation of phenol by water, dissolving in one-third of their weight of alcohol, and mixing with lime. Thus he obtained a pink solution of calcium rosolate and a brown precipitate of calcium brunolate. From the former rosolic acid is precipitated by acetic acid, and purified by repeated solution in milk of lime and precipitation by acetic acid till no more calcium brunolate separates. Finally, by dissolving in alcohol and evaporating, a hard, glassy, orange-coloured mass is obtained, whose valuable dyeing-properties were very emphatically pointed out by Runge, but were first utilized a generation afterwards.

That an oxidation process takes place in this case seems to be proved by the fact that slow heating of the heavy tar-oils with lime in the presence of air much increases the yield of rosolic acid.<sup>1</sup> Angus Smith went even further, by heating phenol, caustic alkali, and manganese dioxide.<sup>2</sup>

#### *Brunolic Acid (?)*

Runge gave this name to an acid which he isolated from the brown precipitate filtered from the solution of calcium rosolate. It was an asphalt-like, glassy mass, undoubtedly a mixture of different chemical compounds.

<sup>1</sup> Tschelnitz, *Wiener Akad. Ber.*, xxiii., p. 169.

<sup>2</sup> *Chem. Gaz.*, 1858, No. 20.

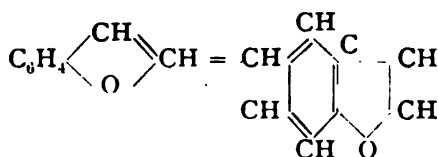


*Cumarone*,  $C_8H_6O$ .

Discovered by Kraemer and Spilker<sup>1</sup> in the fraction of light coal-tar oil boiling between  $168^\circ$  and  $175^\circ$ , and isolated by means of its bromine derivative. They obtained it in the following way:—Into 1 kg. of tar-oil of the just-mentioned boiling-point, freed from phenols and bases, and strongly cooled, 450 g. bromine are slowly introduced, with constant agitation, and avoiding a rise of the temperature above  $0^\circ$ . The oil takes at first a deeply red, afterwards a reddish-brown colour, gives off some hydrogen bromide, and a yellow-white precipitate is formed which is at once separated from the liquid by filtering through glass-wool. After standing twenty-four hours at  $-5^\circ$  to  $-10^\circ$ , again about 80 g. of large prismatic crystals are separated which are re-crystallized from chloroform. Both these crystals and the initially-formed crystalline precipitate are cumarone dibromide,  $C_8H_6Br_2O$ , which fuses at  $86^\circ$ .

According to the Ger. P. 53792 of the Aktien-Gesellschaft für Teer- und Erdöl-Industrie, cumarone is prepared in the pure state from these oils by precipitation with picric acid and decomposition of the picrate.

Fittig and Ebert (*Annalen*, ccxvi., p. 162) prepared it synthetically by distilling cumarilic acid with lime, as a colourless oil, liquid at  $-18^\circ$ , and boiling at  $172^\circ$  (corr.), sp. gr. = 1.096. Its constitution is most probably



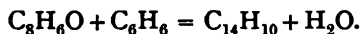
Kompa (*Berl. Ber.*, 1893, p. 2969), effected a smooth synthesis of cumarone from *o*-oxy-*w*-chlorstyrolene by boiling with potassium hydroxide solution. Dennstedt and Ahrens (*Berl. Ber.*, 1895, p. 1331) propose another formula.

In the presence of mineral acids cumarone is polymerised into a solid, resin-like substance of the same composition, *paracumarone* (see below). It combines with picric acid and can be thereby separated from tar-oils; the picrate is split up

<sup>1</sup> *Ber.*, 1890, p. 78; *Z. angew. Chem.*, 1890, p. 119.

by steam in the presence of alkali, and the cumarone passes over with the steam.

In the presence of mineral acids cumarone is polymerized into a resinous body, *paracumarone* (*Ber.*, 1891, Ref. p. 233). Cumarone has been reduced to *hydrocumarone* (Alexander, *Ber.*, 1892, p. 2409) and combined with aniline (Bizzari, *ibid.*, 1891, Ref. p. 369), the latter compound leading over to phenanthrene. This substance is also formed by passing the mixed vapours of cumarone and benzene through a red-hot iron tube:—



Further work in this direction has been done by Dohme (*Amer. Chem. J.*, xiii, p. 29) and Bizzari (*Berl. Ber.*, 1891, Ref. p. 369). Similarly naphthalene and cumarone furnish chrysene. Most probably cumarone plays an essential part in the formation of the higher hydrocarbons of coal-tar. These have been specially investigated by Stoermer (*Chem. Zentr.*, 1900, ii., pp. 1071 and 1079), Stoermer and Boes (*Ber.*, 1900, p. 3013), Kraemer and Spilker (*Ber.*, 1900, p. 2257; 1901, p. 1887).

#### *Paracumarone*

(see above) can be directly separated from the respective tar-oils in an impure state by agitating with 10 per cent. concentrated sulphuric acid, washing the residue with water and alkali, and distilling; the paracumarone remains behind as a more or less coloured resin. It has been proposed to employ it in solution for rendering fabrics, paper, or wood impervious to water.

#### *Methylcumarones.*

Several of these have been prepared synthetically by Stoermer (*Ber.*, 1897, p. 1700), and they have been proved to occur in coal-tar by Stoermer and Boes (*Ber.*, 1900, p. 3013), and Boes (*Chem. Zentr.*, 1901, ii., p. 1226).

The recent investigations on the cumarones and the products obtained by the decomposition of their polymers at high temperatures have proved that the latter occur also in coal-tar (Stoermer, *Chem. Zentr.*, 1901, ii., p. 1226), and have led to the conclusion that most probably coal itself contains polymeric cumarones of a complicated nature, and that the phenols of

## 284 PROPERTIES OF COAL-TAR AND ITS CONSTITUENTS

coal-tar are formed during the heating of the coal in the retort or coke-oven by the decomposition of such cumarones (Russig).

These methyl cumarones are (Stoermer, *Berl. Ber.*, 1897, p. 1700):—

*p*-Methylcumarone,  $\text{CH}_3\text{C}_8\text{H}_5\text{O}$ , colourless oil, boiling at  $197^\circ$  to  $199^\circ$ ; sp. gr. at  $15^\circ = 1.0467$ .

*m*-Methylcumarone,  $\text{CH}_3\text{C}_8\text{H}_5\text{O}$ , boiling at  $195^\circ$  to  $196^\circ$ ; sp. gr. at  $16^\circ = 1.056$ .

*o*-Methylcumarone,  $\text{CH}_3\text{C}_8\text{H}_5\text{O}$ , boiling at  $190^\circ$  to  $191^\circ$ .

*m-p*-Dimethylcumarone, faintly yellow oil, boiling at  $221^\circ$ ; sp. gr. at  $15^\circ = 1.060$ .

*o-p*-Dimethylcumarone, boils at  $221^\circ$  to  $222^\circ$ ; sp. gr. 1.036 at  $16^\circ$ .

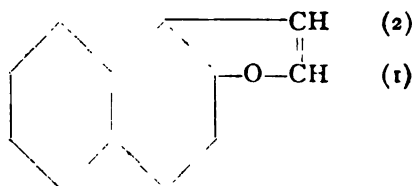
*o-m*-Dimethylcumarone, boils at  $216^\circ$ ; sp. gr. 1.041 at  $16^\circ$ .

Trimethylcumarone, boils at  $236^\circ$ , crystals fusing below  $18^\circ$ ; sp. gr. 1.0205 at  $21^\circ$ .

*p*-Ethylcumarone, boils at  $217^\circ$  to  $218^\circ$ .

### $\beta$ Naphthofuran, $\text{C}_{12}\text{H}_8\text{O}$ ,

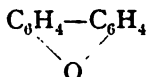
has been found in coal-tar by Boes (*Chem. Zentr.*, 1902, i., p. 1356). White needles fusing at  $50^\circ$  to  $51^\circ$ , boiling at  $284^\circ$  to  $286^\circ$  C. Constitution:



### Diphenylene Oxide, $\text{C}_{12}\text{H}_8\text{O}$ ,

obtained by Lesimple, Behr and van Dorp, Graebe, and other chemists from phenol and other materials. Afterwards discovered in coal-tar by Kraemer and Weissgerber (*Ber.*, 1901, p. 1662), after Kraemer and Spilker had made its presence therein probable already in 1890 (*Ber.*, 1890, p. 3281). It is found in the crude fluorene fraction of heavy coal-tar in about the same quantity at its isomers, cumarones, in the correspond-

ing fraction of light oil, and is most easily ascertained by fusing fluorene with caustic potash which yields 12 per cent. of its derivative diphenol,  $C_{12}H_{10}O_2$ . Diphenylene oxide forms snow-white flakes, with a blue fluorescence, melting at  $86^\circ$  to  $87^\circ$  and boiling at  $275.5$  to  $276^\circ$ . Its formula is:—



It is very stable against oxidizing and reducing agents, and does not acquire any colour in daylight. Its presence in the high-boiling fractions of coal-tar is a great impediment to the preparation of fluorene, phenanthrene, etc., in the pure state.

*Dioxydiphenyl,  $C_{12}H_{10}O_2$ ,*

was found by Spilker (Ger. P. of the Aktien-Gesellschaft für Teer- und Erdöl-Industrie, Nos. 111359, 124150, and 130679) among the products of the carbazol melt in the purification of anthracene. Kraemer and Weissgerber (*Ber.*, 1901, p. 1662) found it among the products of the alkaline fluorene melt. This body had been previously described by Barth (*Ann. Chem.*, clvi., p. 96), Limpricht (cclxi., p. 332), Hodgkinson and Matthews (*J. Chem. Soc.*, 1882, i., p. 168) as *o-o*-biphenol and 2, 2'-dioxybiphenyl. Diels and Bibergeil (*Berl. Ber.*, 1902, p. 303) found its fusing-point at  $109^\circ$ , the boiling-point at  $325^\circ$  to  $326^\circ$ . It is abundantly soluble in water and forms with it a hydrate, fusing at  $70^\circ$  to  $71^\circ$ .

*Xanthene,  $C_{13}H_{10}O$ ,*

the anhydride of *o*-dioxydiphenyl-methane, has not yet been isolated from coal-tar, but according to Weger (*loc. cit.*) its presence is made probable by the proof of the existence of *o*-dioxydiphenylmethane.

SULPHURETTED COMPOUNDS.

*Hydrogen sulphide,  $H_2S$ .*

*Ammonium Sulphide,  $(NH_4)_2S$ .*

*Ammonium sulphocyanide,  $(NH_4)NCS$ .*

*Sulphur dioxide,  $SO_2$ .*

All of these must occur in coal-tar, as they are always present in gas-liquor (*cf.* the preceding chapter).

*Carbon disulphide, CS<sub>2</sub>.*

Boiling-point 47°. Sp. gr. 1.272. It was found in crude benzol by Vincent and Delachanal;<sup>1</sup> it had often previously been assumed to exist in tar, as it is always found in illuminating-gas. Watson Smith found 6 per cent. of CS<sub>2</sub> in the first runnings of rectified benzol from London gas-tar. H. L. Greville prepared it on the large scale from the calcium-sulphide purifiers of gas-works.<sup>2</sup>

Ahrens (*Chem. Zentr.*, 1906, i., p. 510) found in the first runnings from coal-tar a sulphuretted compound similar to, but not identical with carbon disulphide.

*Carbon oxysulphide, COS,*

has not yet been found in tar, but is sure to exist dissolved in it, since all conditions for its formation are present. It is a colourless gas, smelling of carbonic anhydride and slightly of hydrogen sulphide, of very faintly acid reaction. It is extremely inflammable, and with sufficient oxygen yields CO<sub>2</sub> and SO<sub>2</sub>; with insufficient oxygen, or on cooling, it yields only CO<sub>2</sub> and S:  $\text{COS} + \text{O} = \text{CO}_2 + \text{S}$ .

*Thiophen, C<sub>4</sub>H<sub>4</sub>S.*

This substance was discovered in commercial benzol by Victor Meyer in 1883,<sup>3</sup> and thoroughly examined by this chemist, his disciples, and other chemists during the following years, so that V. Meyer could as early as 1888 publish a book, *Die Thiophengruppe*, giving a synopsis of over a hundred various publications. Thiophen occurs in every variety of coal-tar benzol, up to 0.5 per cent. (also in lignite oils<sup>4</sup>), and is the cause of some colour-reactions previously ascribed to benzol itself by Baeyer, Classen, and Laubenheimer. It can be isolated by the peculiarity that it is more soluble in concentrated sulphuric acid than benzol. According to the prescription of Schulze (*Berl. Ber.*, xviii., p. 697), commercial "pure" benzol is well agitated with one-tenth part concentrated sulphuric acid, the black acid-tar is separated, diluted with

<sup>1</sup> *Comptes rend.*, lxxxvi., p. 340.

<sup>2</sup> *J. Soc. Chem. Ind.*, 1883, p. 488.

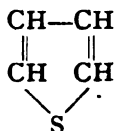
<sup>3</sup> *Berl. Ber.*, xvi, p. 1465.

<sup>4</sup> *Ibid.*, xxviii., p. 493

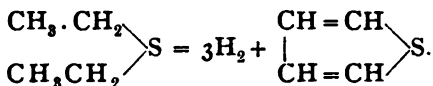
water and steam passed through, when crude "thiophen" (containing 30 per cent. pure thiophen) distils over.

This is dissolved in 100 parts petroleum-spirit, and the solution is agitated with one-tenth of its volume of concentrated sulphuric acid, which takes out the thiophen as a sulphonic acid. The latter is converted into a lead salt, and this is distilled with one-fourth of its weight of ammonium chloride, pure thiophen passing over.

Thiophen has also been synthetically prepared by Victor Meyer and Sandmeyer<sup>1</sup> from ethylene or acetylene and boiling sulphur, and by Volhard and Erdmann<sup>2</sup> from sodium succinate and phosphorus trisulphide; also in several other ways. Its rational formula is:—



Its formation in the distillation of coal in the gas-retort is explained by the observation of Victor Meyer and A. Calm (*Ber.*, xviii., p. 217) that it is also formed when coal-gas is passed over pyrites or ethyl sulphide contained in a red-hot tube:



Thiophen is a colourless mobile liquid, of a faint, not very characteristic smell. It boils at 84°; sp. gr. at 18° = 1.062. Its chemical properties are a real "mimicry" of those of benzene. It is insoluble in water, miscible in all proportions with benzene and petroleum-spirit, soluble in concentrated sulphuric acid with dark brown colour. Alkalis do not change it; it can be distilled over sodium without being decomposed. Nitric acid acts violently upon it, and forms a nitro-compound which is easily reduced to an amide-compound. It gives several colour-reactions; one of the best is the blue colour produced by nitrosulphuric acid (Liebermann, *Ber.*, 1887, p. 3231).

The methods for estimating and removing thiophen will be described in Chapter XI.

<sup>1</sup> *Berl. Ber.*, xvi., p. 2176.

<sup>2</sup> *Ber.*, xviii., p. 454.

According to experiments made by Rambousek (*Concordia*, 1910, p. 450) air containing 0.03 to 0.05 parts in 1000 can be inhaled for an hour without producing any symptom of poisoning.

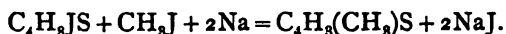
*Methylthiophen (Thiotolen)*,  $C_6H_6S$ ,

discovered by V. Meyer and Kreis (*Ber.*, xvi., pp. 1624, 2970; xvii., p. 787) in commercial toluol. There are two isomers:

$\alpha$  *Thiotolen* boils at  $112^\circ$  to  $113^\circ$ .

$\beta$  *Thiotolen* also boils at  $113^\circ$ ; sp. gr. of the mixture at  $18^\circ = 1.019$ . The thiotolens cannot be extracted from toluol by means of sulphuric acid, but this can be done by treating the toluol with iodine and mercuric oxide at the ordinary temperature, whereby thiotolen iodide is formed which can be reduced by sodium and absolute alcohol.

$\alpha$  *Thiotolen* boils at  $112^\circ$  to  $113^\circ$  and on oxidation by potassium permanganate yields  $\alpha$  thiophenic acid of the fusing-point,  $126.5$ . If it is mixed with a solution of phenanthrene-quinone in glacial acetic acid, and sulphuric acid is added, with good cooling, a dark green colour is produced; if the liquid is now diluted with water, well cooling, it imparts a fine *purple colour* to ether (Laubenheimer's reaction). It has been synthetically prepared by Fittig's method from thiophene iodide, methyl iodide, and sodium:



Kues and Paal (*Ber.*, xix., p. 555) have effected its synthesis from levulinic acid and phosphorus trisulphide.

$\beta$  *Thiotolen* also boils at  $113^\circ$ , but on oxidation with permanganate it yields  $\beta$ -thiophenic acid, fusing at  $136^\circ$ . When treated with phenanthrene-quinone, etc., as described *supra*, it imparts to ether a *blue* colour. It has been synthetically obtained by Volhard and Erdmann by distilling sodium pyrovinat with phosphorus trisulphide.

*Dimethylthiophen (Thioxen)*,  $C_8H_8S$ .

The mixture of the various isomeric thioxens was obtained by K. E. Schulze (*Ber.*, xvii., p. 3852) from xylol-purifying acid by distillation with steam. Messinger (*ibid.*, xviii., p. 563 and 1636) prepared it in a pure state. Kitt (*ibid.*, xxviii., p. 1807)

and especially Keiser (*ibid.*, xxix., p. 2560) proved that the thioxen from coal-tar consists of several isomers. Four isomers are possible, all of which have been synthetically obtained, viz. :—

(1)  $\alpha$ - $\alpha$  thioxen (Ruffi, *Ber.*, xx., p. 1748) and Paal (*ibid.*, xviii., p. 2252). Boils at  $135^{\circ}$  to  $136^{\circ}$  and in Laubenheimer's reaction it gives a strong reddish-purple colour.

(2)  $\alpha$ - $\beta^1$ -thioxen (*metathioxen*), prepared by Zelinski (*ibid.*, xx., p. 2018). Boils at  $137^{\circ}$  to  $138^{\circ}$  and yields a dark purple colour in Laubenheimer's reaction.

(3)  $\alpha$ - $\beta$ -thioxen (*orthothioxen*), prepared by Paal and Puschel (*ibid.*, xx., p. 2559) and Grünwald (*ibid.*, xx., p. 2585). Boils at  $136^{\circ}$  to  $137^{\circ}$ ; yields a purple colour in Laubenheimer's reaction.

(4)  $\beta$ - $\beta$ -thioxen, prepared by Zelinski (*ibid.*, xxi., p. 1835). Boils at  $136^{\circ}$  to  $137^{\circ}$ , gives the same reaction as the last.

#### *Trimethylthiophen*, $C_7H_{10}S$ .

The  $\alpha$ - $\beta$ - $\beta$  modification has been synthetically obtained by Zelinski (*Ber.*, xx., p. 2025). Boils at  $160^{\circ}$  to  $163^{\circ}$ . Not yet found in coal-tar, but sure to exist there. The same holds good of

#### *Tetramethylthiophen*, $C_8H_{12}S$ ,

prepared by Zelinski (*Ber.*, xxi., p. 1837). Boils at  $182^{\circ}$  to  $184^{\circ}$ .

#### *Derivatives of Thiophen.*

Very many of these exist, like those of benzene, but none of them have as yet been isolated from coal-tar. We mention *biophen*,<sup>1</sup>  $C_4H_4S_2$ ; *dithienyl*,<sup>2</sup>  $C_8H_6S_2$ ; *trithienyl*,<sup>3</sup>  $C_{12}H_8S_3$ ; *thionaphthene*,<sup>4</sup>  $C_8H_6S$ ; and *thiophptene*,<sup>5</sup>  $C_8H_4S_2$ .

#### *Diphenylene sulphide*, $C_{12}H_8S$ ,

is indicated by Kraemer and Weissgerber (*Ber.*, 1901, p. 1662), as occurring in the high-boiling fractions of coal-tar, together

<sup>1</sup> Levy, *J. Chem. Soc.*, lxii., p. 216.

<sup>2</sup> Schmidt and Schulz, *Ber.*, xvii., p. 789.

<sup>3</sup> Renard, *Comptes rend.*, cxii., p. 79.

<sup>4</sup> Gattermann and Lockhart, *Ber.*, xxvii., p. 2808.

<sup>5</sup> Biedermann and Jacobson, *ibid.*, xix., p. 2444.



with the analogous oxide (p. 284), but it has not been isolated in the pure state. It seems to be the cause of the reddening of crude fluorene and phenanthrene when exposed to sunlight.

### *Mercaptans,*

or similar sulphuretted compounds having a disagreeable smell, are probably present in coal-tar. The "alliol" of which Mansfield stated the boiling-point to be  $70^{\circ}$  to  $80^{\circ}$ , and of which he obtained 30 to 40 g. from 50 litres of tar, is perhaps a mixture of such compounds, although carbon disulphide might be also contained in it. Vohl (*Dingl. polyt. J.*, clxviii., p. 49) has found, in crude benzene, sulphuretted bodies boiling below  $80^{\circ}$ .

		boils at	Sp. gr.
Methyl mercaptan,	$\text{CH}_3 \cdot \text{SH}$ ,	$20^{\circ}$	
Methylic sulphide,	$(\text{CH}_3)_2\text{S}$ ,	$41^{\circ}$	0.845
Ethyl mercaptan,	$\text{C}_2\text{H}_5 \cdot \text{SH}$ ,	$36^{\circ}$	0.831
Ethylic sulphide,	$(\text{C}_2\text{H}_5)_2\text{S}$ ,	$91^{\circ}$	0.852
Etc.			

*Cf.* also Ahrens (*Chem. Zentr.*, 1906, i., p. 510).

### *Free Sulphur*

has been found by Kehlstadt<sup>1</sup> in the distillates of coal-tar. It is probably formed from  $\text{SO}_2$  and  $\text{H}_2\text{S}$  under the action of water.

## NITROGENIZED COMPOUNDS.

### A. BASIC.

#### *Ammonia, $\text{NH}_3$ ,*

has been already mentioned as ammonium sulphide and sulphocyanide. It occurs also as carbonate, and forms the most important constituent of gas-liquor. A colourless gas, of the well-known pungent smell, sp. gr. 0.5888, condenses at  $-40^{\circ}$  to a liquid, and solidifies at  $-70^{\circ}$ . Its ready solubility in water, the strongly basic properties of this solution, etc., are universally known.

<sup>1</sup> *Ber.*, 1880, p. 1345.

*Substituted Ammonias*

of the fatty series probably occur in gas-liquor, and consequently in tar. We shall only quote the boiling-points, etc., of the lowest members.

*Methylamine*,  $\text{NH}_2(\text{CH}_3)$ , is a gas. One vol. water at  $12^\circ$  absorbs 1040 vols. of it. It is inflammable, and smells both of fish and ammonia.

*Dimethylamine*,  $\text{NH}(\text{CH}_3)_2$ , boils at  $8^\circ$  to  $9^\circ$ ; readily soluble in water. Smell strongly ammoniacal.

*Trimethylamine*,  $\text{N}(\text{CH}_3)_3$ , boils at  $9^\circ.3$ ; readily soluble in water. Smells of ammonia and herring-brine, in which it occurs abundantly.

*Ethylamine*,  $\text{NH}_2(\text{C}_2\text{H}_5)$ , boils at  $18^\circ.7$ ; readily soluble in water.

*Diethylamine*,  $\text{NH}(\text{C}_2\text{H}_5)_2$ , boils at  $57^\circ.5$ ; readily soluble.

*Triethylamine*  $\text{N}(\text{C}_2\text{H}_5)_3$ , boils at  $91^\circ$ ; little soluble.

The higher members and the extremely numerous mixed amines cannot be noticed here.

Köhler (*Dingl. polyt. J.*, 1889, part 2) discusses the occurrence of substituted ammoniæ in coal-tar.

Trobridge (*J. Soc. Chem. Ind.*, 1909, p. 230) describes the basic compounds found in the tar from Otto-Hilgenstock coke-ovens.

*Cespitine*,  $\text{C}_6\text{H}_{13}\text{N}$ ,

is a base of unknown constitution, isomeric with amylamine and boiling at the same temperature ( $95^\circ$ ). It was discovered by Church and Owen. A colourless oil of strong smell, but not so disagreeable as that of amylamine; readily soluble in water, but not in concentrated solution of caustic soda. Lighter than water. Church and Owen suppose it to contain a trivalent radical  $(\text{C}_5\text{H}_{13})'''$ . Fritzsche thought he had found it in coal-tar, but Goldschmidt and Constam consider Fritzsche's cespitine to be their pyridine hydrate (see below). This agrees with the observations made in my laboratory.

*Aniline*,  $\text{C}_6\text{H}_5 \cdot \text{NH}_2$ 

*Syn.* phenylamine, amidobenzene, etc. Discovered in 1826 by Unverdorben; found in coal-tar in 1834 by Runge (who

called it kyanol). A colourless liquid, rapidly turning yellow, then red or brown, of a peculiar faint smell and burning taste. Solidifies at  $-8^{\circ}$  (according to some statements, not even at  $-20^{\circ}$ ) and boils at  $182^{\circ}$ ; the vapour burns readily. Sp. gr. at  $16^{\circ}=1.020$ . It possesses poisonous properties, especially for smaller animals. Water dissolves about 2 per cent.; and aniline dissolves some water itself. Readily soluble in alcohol, ether, acetone, carbon disulphide, hydrocarbons, etc. It dissolves sulphur, phosphorus, camphor, rosin. The aqueous solution has only faintly basic properties, and does not even turn red litmus blue; but at a higher temperature it expels ammonia from its salts, whilst in the cold it is precipitated by ammonia. With chloride of lime it turns purple (this has been explained by Raschig, *Z. angew. Chem.*, 1907, p. 2071, by the formation of an indophenol); with potassium bichromate and sulphuric acid, blue. Its aqueous solutions precipitate the oxides from the salts of iron, zinc, and aluminium. With the mineral acids it forms salts which are readily soluble in water and alcohol and readily crystallize; they are white when quite pure, but redden quickly in the air and acquire a faint smell.

Immense as is the importance of the aniline made from coal-tar benzol, its direct occurrence in coal-tar is of small moment. In that substance it is practically only an impurity, from which the hydrocarbons must be freed by acid treatment; neither does it seem feasible to extract at a profit the small quantity present in coal-tar.

Probably the basic substance which former inquirers extracted from coal-tar, and which yielded the characteristic reactions of aniline, contained only a small percentage of real aniline.

According to Watson Smith,<sup>1</sup> aniline occurs in all distillates of coal-tar, principally (as might be expected from its boiling-point) in the light oils of sp. gr. 0.900 to 1.000. Eugen Oehler (*Z. angew. Chem.*, 1899, p. 561) found it also in browncoal tar-oils.

The *homologues of aniline* (toluidine, etc.) have not yet been found in coal-tar, but it is most likely that they are contained in it.

<sup>1</sup> *J. Chem. Soc.*, 1874, p. 853.

*Pyridine Series.*

This series includes a number of bases of the formula  $C_nH_{2n-3}N$ , from pyridine to viridine. They are characterized by the "pyridine nucleus," which is quite analogous to the benzene nucleus, but contains N in lieu of a threevalent group CH. They are very stable, even towards oxidizing agents. They occur chiefly in the tar-oils of sp. gr. 0.900 to 0.990.

The pyridine bases found in coal-tar have been investigated by A. W. Hofmann (*Ber.*, 1881, p. 1497), who describes as a general reaction for these bases the characteristic smell which they produce when treated with methyl iodide and caustic potash. These bases and the quinoline series are of very great importance, since it has been proved that the natural alkaloids are derivatives of pyridine, and some compounds, very useful for medical purposes (*e.g.*, antipyrine), have been synthetically produced from them.

Stöhr (*J. prakt. Chem.*, xliii, p. 153) obtained the bases of this series synthetically by the action of ammonium sulphate on glycerine.

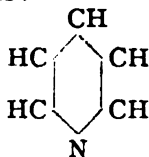
*Pyridine,  $C_5H_5N$ .*

Discovered by Anderson in bone-tar, by Greville Williams in coal-tar. Häussermann (private communication) found as much as 0.1 per cent. in commercial 50-per-cent. benzol, and 0.25 per cent. in the toluol made from this. Ahrens and Dennstedt (*Ber.*, 1894, p. 601) found it in coal-gas; Rosenthal (*Chem. Zeit.*, 1890, p. 870) in oil from lignite; Loof (*Ber.*, 1893, Ref., p. 710) in wood-tar; Haitinger (*Sitz. Ber. Wien. Akad. Wiss.*, July 1882) and Asboth (*Chem. Zeit.*, 1889, p. 871) in some samples of commercial amyl alcohol; Monari and Scoccianti (*Gazz. Chim.*, xxv. (1), p. 115; *Berl. Ber.* 1895, Ref., p. 329) in the products from roasting coffee; Garrett and Smythe (*J. Soc. Chem. Ind.*, 1902, p. 398) in small quantities in the bases of Scotch shale-oil.

The synthesis of pyridine has not yet been effected to any notable extent. Ramsay (*Berl. Ber.*, x., p. 736) asserted having found it on passing acetylene and cyanhydric acid through red-hot tubes, formed by the equation  $2C_2H_2 + CNH = C_5H_5N$ , but Ljubawin (Beilstein, 3rd ed., iv., p. 105) could not confirm that reaction. It is important for recognising the

relation between pyrrol and pyridine that Dennstedt and Zimmermann (*Berl. Ber.*, 1885, p. 3317) converted pyrrol into pyridine by heating it with potassium alchoolate and methylene iodide.

Its structural formula is :



and it presents very great interest as the starting-point for a long series of important derivatives.

Pyridine is a colourless, mobile liquid of penetrating smell. Sp. gr. at  $0^{\circ}$  = 0.9858; boils at  $116^{\circ}.7$  (Anderson) or  $115^{\circ}$  (Thenius and Weger). It solidifies at  $-42^{\circ}$ . Sp. gr. 0.978 at  $15^{\circ}$ . Miscible with water in all proportions, and reprecipitated by caustic potash or soda. Turns red litmus blue, gives off white vapours with hydrochloric acid, precipitates the salts of zinc, iron, manganese, and aluminium. Resists the action of fuming nitric and chromic acids. With the acids it forms stable salts readily soluble in water and alcohol, which can be dried at  $100^{\circ}$ , and hardly turn brown in the air. Vongerichten (*Ber.*, 1899, p. 2571) has described a reaction on pyridine by  $\alpha$  dinitrochlorbenzene. Helch (*Chem. Centr.*, 1902, ii., p. 146) describes some reactions for distinguishing pyridine from other bases. Braeutigam (*Chem. Centr.*, 1902, ii., p. 466) states that by a solution of tannic acid in 25 parts of water very little pyridine (1 : 6000) can be proved by the formation of a precipitate.

Pyridine, in a solution of 1 : 700, coagulates albumina, and is therefore a strong bactericidal agent. It is recommended as a healing agent for the stings of hornets, and even as a remedy against the tendency to drink!

Pyridine, according to Bedson (*J. Soc. Chem. Ind.*, 1908, p. 147) and Donath (*Z. angew. Chem.*, 1906, p. 657), has a solvent action on the "bituminous" constituents of coal-tars, leaving a residue of almost coke-like character. This property may possibly be turned to important technical purposes, if a proper use is found for the substances thus extracted from coal, for instance for the purification of anthracene.

Goldschmidt and Constam (*Berl. Ber.*, 1883, p. 2976) found in the mixture of bases obtained from coal-tar a molecular compound of pyridine and water,  $C_6H_5N, 3H_2O$ , sp. gr. 1.0219, boiling at  $92^\circ$  to  $93^\circ$ , smelling similarly to pyridine, and perhaps identical with "cespitine."

The physico-chemical properties of mixtures of pyridine and water have been thoroughly examined by Hartley, Thomas, and Applebey (*J. Chem. Soc.*, 1908, xciii, pp. 538, 561). Mackenzie (*J. Ind. Eng. Chem.*, 1909, p. 360) states that commercial pyridine always contains picolines and water. The latter forms with pyridine a definite hydrate, boiling at  $94.4^\circ$  C. This hydrate has very little solvent action on bituminous matters, and its presence materially impairs the solvent powers of pyridine.

*Picoline (Methyl-pyridine)*,  $C_6H_7N = C_6H_4 \cdot CH_3 \cdot N$ .

*Syn. odorine.* Isomeric with aniline. Discovered by Unverdorben in bone-oil by Anderson in coal-tar. Ihlder (*Z. angew. Chem.*, 1904, pp. 523 and 1670) and Frese (*ibid.*, 1903, p. 11) found picolines in lignite-tar, Einhorn and Gilbody (*ibid.*, 1893, p. 1414) in tar from bituminous schists. A colourless, mobile liquid of penetrating smell. Boils at  $135^\circ$ ; sp. gr. at  $0^\circ = 0.9613$  (Anderson), at  $22^\circ = 0.933$  (Thenius). Its solubility, salts, and basic properties resemble those of pyridine. Coal-tar picoline is no doubt  $\alpha$  picoline, viz., orthomethyl-pyridine (Goldschmidt and Constam); but  $\gamma$  pyridine is present in small quantities (K. E. Schulze, *Ber.*, 1887, p. 413), and Mohler (*ibid.*, 1893, p. 1414) proved also the presence of  $\beta$  picoline.  $\gamma$  picoline has also been isolated from these oils by Ahrens (*Ber.*, 1905, p. 155).

The isomeric picolines are :

$\alpha$ -picoline, boils at  $133.5$  (corr.), sp. gr. 0.952 at  $10^\circ$ .

$\beta$ -picoline, boils at  $143.5$  (corr.), sp. gr. 0.9726.

$\gamma$ -picoline, boils at  $142.5$  to  $144.5$  (corr.), sp. gr. 0.9742.

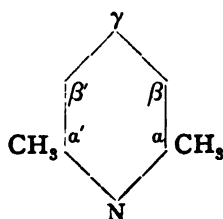
$\alpha$ -picoline can be obtained approximately pure by fractional distillation (Weger). According to Mackenzie (*loc. cit.*) the picolines are even better solvents for india-rubber than pyridine, even better than carbon disulphide.

*Dimethyl-pyridines (Lutidines), C<sub>7</sub>H<sub>9</sub>N.*

The first lutidine was found in tar-oils by Anderson (*Trans. Roy. Soc., Edin.*, xx., p. 246) in 1851, and other bases of the same composition were discovered in different materials by Greville Williams (*Chem. Soc. Quart. J.* [3], vii., p. 97); Church and Owen (*Phil. Mag.* [4], xx., p. 110), and Thenius (Inaug. Diss., Göttingen, 1861). Much later it was proved by the work of Ladenburg, of Lunge and Rosenberg, and by K. E. Schulze, that these bases are mixtures of isomers, of which 6 dimethyl-pyridines and 3 ethyl-pyridines are possible, and mostly also known.

All six theoretically possible isomers are known.

*α α' lutidine,*



has been isolated from coal-tar oils by Lunge and Rosenberg (*Berl. Ber.*, 1887, p. 409), by K. E. Schulze (*ibid.*, 1893, p. 1414), and by Ahrens and Garbow (*Ber.*, 1904, p. 2062); from the tar of bituminous shale by Einhorn and Gilbody (*Z. angew. Chem.*, 1893, p. 1414. Boils at 142°, smells like peppermint.

*α γ lutidine* has been isolated by the same. Smells like cucumber; boils at 156° to 157°.

*α β lutidine* has been found by Ahrens (*Chem. Zentr.*, 1906, i., p. 510) in the commercial "*α β* Picoline" sold by the Erkner works. It boils at 162° to 163°; its picrate melts at 183°, and is almost insoluble in alcohol.

*α β' lutidine* has been proved in coal-tar oils, in the fraction boiling between 150° to 170°, by Lunge and Rosenberg.

*β γ lutidine* was isolated from coal-tar by Ahrens (*Ber.*, 1896, p. 2999); boils at 163°.5 to 164°.5.

*β β' lutidine* has been only synthetically produced; boils at 169° to 170°.

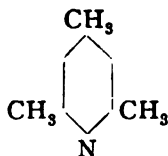
The 3 ethyl-pyridines have been obtained by synthesis;

their presence in coal-tar is not probable. Boiling-point  $164^{\circ}$  to  $166^{\circ}$ .

*Collidines*,  $C_8H_{11}N$ .

Twenty-two isomers are possible, of which only a few have been proved in coal-tar.

The *symmetrical collidine* ( $\alpha$ - $\gamma$ - $\alpha'$  trimethyl-pyridine),



was found by Lunge and Mohler (*Ber.*, 1888, p. 1006) in coal-tar, after having been previously synthetically prepared by Kraemer (*Ber.*, 1870, p. 262) from ethylidene bichloride and ammonia. Boils at  $171^{\circ}$  to  $172^{\circ}$ . More soluble in cold than in hot water.

$\alpha'$   $\beta$   $\gamma$  trimethyl-pyridine was found in coal-tar, with the former, by Ahrens (*Ber.*, 1896, p. 2999). Boils at  $165^{\circ}$  to  $168^{\circ}$ .

*Parvolines*,  $C_9H_{13}N$ .

Six of the 54 possible isomers are known; in coal-tar only tetramethyl-pyridines seem to be present (Dürkopf and Göttisch, *Ber.*, 1890, p. 1110). The parvoline boiling at  $188^{\circ}$ , stated by Thenius to occur in coal-tar, was not found by Ahrens (*Ber.*, 1895, p. 795), but he obtained another, boiling at  $232^{\circ}$  to  $234^{\circ}$ .

*Coridines*,  $C_{10}H_{15}N$ .

That indicated by Thenius, boiling at  $211^{\circ}$ , was not found by Ahrens; the base obtained by Thenius was probably a mixture. A similar base has been found by Zaloziecki (*Ber.*, 1892, p. 732) in Galician petroleum.

*Rubidine*,  $C_{11}H_{17}N$ .

Discovered by Thenius. A colourless oil of faint smell, boils at  $230^{\circ}$ , turns viscid at  $-17^{\circ}$ , insoluble in water, soluble in alcohol, ether, etc. Sp. gr. at  $22^{\circ} = 1.017$ . It precipitates some oxides from their salts. Its salts do not crystallize well,



and turn pink in the air; chloride of lime turns it pink; it stains pine-wood moistened with hydrochloric acid a red colour.

*Viridine*,  $C_{12}H_{19}N$ .

Discovered by Thenius. A yellowish oil, of sweet aromatic smell; boils at  $251^{\circ}$ , and is not solidified at  $-17^{\circ}$ . Does not colour in the air; very little soluble in water. Sp. gr. at  $22^{\circ} = 1.024$ .

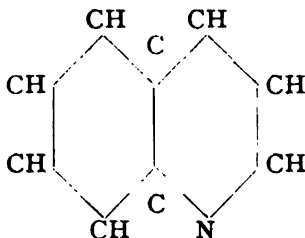
Neither rubidine nor viridine have been found by Ahrens in coal-tar, and their existence cannot be considered proved.

*Quinoline Series.*

Quinoline contains a benzene nucleus attached to a pyridine nucleus. It was first investigated by Greville Williams (*J. Chem. Soc.* [2], i., p. 375), and has recently become of much more importance, since some of its members have been synthetically prepared and have found practical application.

The theoretical study of quinoline has been principally advanced by Körner (*Gazz. Chim.*, xl., p. 548).

Körner considers them as derivatives of naphthalene, in which one of the CH groups is substituted by nitrogen. He



finds this view on the synthesis from allylaniline and hydrocarbostyryl, and on the fact that quinoline, on being oxidized under certain conditions, the benzene nucleus being split up, yields a pyridine-carbonic acid corresponding to phthalic acid.

The synthesis of quinoline and its derivatives was affected by Skraup from glycerine, nitrobenzene, and sulphuric acid, (*Monatsh.*, i., p. 317; ii., p. 141); by Döbner and Miller (*Ber.*, xiv., p. 2812; xv., p. 3075; xvi., p. 2464) from aniline, paraldehyde and hydrochloric acid; by Friedländer (*Ber.*, xv., p. 2573;

xvi., p. 1834) from amidobenzaldehyde, acetaldehyde, and sodium-hydrate solution; by Knorr (*Ber.*, xvi., p. 2595) from aniline and aceto-acetic ether.

*Quinoline or Leucoline*,  $C_9H_7N$ .

Discovered in 1834 by Runge. It was assumed for a long time that the "leucoline" found in coal-tar was not the same as, but only isomeric with, the "quinoline" obtained from cinchonine; but it was shown by Hoogewerf and van Dorp (*Ber.*, 1883, p. 425) that they are identical. It boils at  $239^\circ$  to  $240^\circ$ , and has a specific gravity of 1.081, a penetrating smell, and burning taste. It is little soluble in water, readily in alcohol and ether. With potassium-mercuric iodide it yields, even in very dilute solutions (1 : 3500), a yellowish-white precipitate, which on addition of hydrochloric acid turns into amber-coloured needles. Found by Doebner (*Ber.*, 1895, p. 306) also in lignite oils and synthetically produced by Baeyer (*Ber.*, xii., p. 1320) from hydrocarbostyryl.

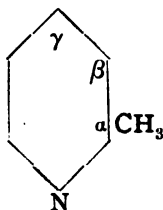
*Isoquinoline*,  $C_9H_7N$ .

Found by Hoogewerf and van Dorp together with the preceding; boils at  $236^\circ$  to  $237^\circ$ ; fuses at  $20^\circ$  (Weger). A new communication on that base by Weissgerber (*Berl. Ber.*, 1914, p. 3175) confirms their results.

*Methylquinolines (Quinaldines)*,  $C_{10}H_9N$ .

Of the nine possible isomers, most have been synthetically produced. The following have been proved to exist in coal-tar:—

*a methylquinoline (quinaldine)*,



forms, according to E. Jacobsen and Reimer (*Ber.*, 1883, p. 1082),

25 per cent. of commercial coal-tar quinoline; synthetically produced by Doebner and v. Miller (*Ber.*, 1881, p. 2812). Colourless liquid, strongly refractive, boils at  $238^{\circ}$  to  $239^{\circ}$ .

$\gamma$  *methylquinoline* (*lepidine*), first obtained by Greville Williams from cinchonine. Smells like quinoline, boils at  $256^{\circ}$  to  $258^{\circ}$ . Probably identical with the *iridoline* found by Greville Williams<sup>1</sup> in coal-tar, and stated to boil between  $250^{\circ}$  and  $257^{\circ}$ ; sp. gr. at  $15^{\circ} = 1.072$ .

*Dimethylquinolines*,  $(\text{CH}_3)_2\text{C}_9\text{H}_5\text{N}$ .

One of these has been found in coal-tar by Greville Williams and described as *cryptidine*, boiling at  $274^{\circ}$ ; it is probably identical with the 2, 3 or 3, 4 dimethylquinoline of Berend (*Ber.*, xvii., pp. 1489 and 2716).

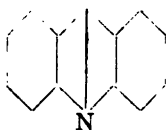
*Acridine*,  $\text{C}_{13}\text{H}_9\text{N}$ .

Discovered by Graebe and Caro (*Ber.*, 1872, p. 15) in crude anthracene; reinvestigated by Riedel (*Ber.*, 1883, p. 1611) and Bernthsen and Bender (*ibid.*, p. 1802). Obtained by extracting crude anthracene with dilute sulphuric acid, precipitating by potassium chromate, purifying the chromate by recrystallization, precipitating the base by ammonia, and recrystallizing the same from hot water. Or the hydrochlorate is recrystallized and decomposed by ammonia. Acridine crystallizes in orthorhombic prisms, which are colourless if very small, brown if rather large. It fuses at  $111^{\circ}$  (at  $107^{\circ}$ , according to Weger), distils above  $360^{\circ}$  without change, sublimes at  $100^{\circ}$ , and is carried over by aqueous vapour. It is sparingly soluble in cold, more soluble in hot water, and readily so in ether, alcohol, carbon disulphide, and hydrocarbons. It possesses a faint alkaline reaction; but even very dilute solutions of its salts cause acute stinging when applied to the skin; its dust in very minute quantity causes most violent sneezing. (This property of acridine is sometimes very inconvenient to the workmen in subliming crude anthracene, especially in summer-time, when they have to protect the skin of the face by rubbing fat upon it.) It has a strong destroying action on infusoria, especially in sunlight (Raab, *Chem. Zentr.*, 1900, i., pp. 491, 1135). Sulphuric

<sup>1</sup> *Jahresber.*, 1855, p. 550.

acid attacks acridine only at  $200^{\circ}$ ; hydrochloric acid and caustic potash do not attack it even at  $280^{\circ}$ ; while zinc-dust, soda-lime, and many oxidizing agents do not act upon it at all. Nitric acid forms nitro-compounds. With the acids it forms salts of a yellow colour, easily soluble and crystallizable; their dilute solutions fluoresce strongly with a blue colour, more concentrated ones green, but very concentrated solutions do not show any fluorescence.

Acridine has been synthetically produced by Bernthsen (*Ber.*, xvi., p. 1808) and E. Fischer (*Ber.*, xvi., p. 1820; xvii., p. 101); *cf.* Riedel (*Ber.*, xvi., p. 1609). Graebe proved its structural formula to be:

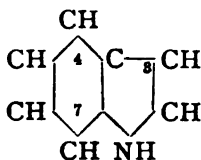


*Methylacridines* have as yet only been obtained by synthesis; *cf.* Bernthsen and Bender (*Ber.*, xvi., p. 1808) and Graebe (*Ber.*, 1894, Ref. p. 641).

The *hydrides* of acridine have been found in coal-tar by Kraemer and Spilker (*Ber.*, 1896, p. 561), methylacridine hydride by Boes, who (*Chem. Zeit. Rep.*, 1902, p. 308) has also found hydroacridine in anthracene oil, by extracting it with sulphuric acid and precipitating with water or extracting with ether. This compound has no basic properties.

### *Indol*, $C_8H_7N$ .

This weak base, occurring in small quantities in human faeces, and formed in abundant quantities on heating many indigo compounds with zinc dust or tin and hydrochloric acid (Bayer, *Ann. Chem.*, Suppl., vii., p. 56), has been recently found in that portion of coal-tar oils which boils between  $220^{\circ}$  and  $270^{\circ}$ . Its constitution is:



It forms shining leaflets, fusing at  $52^{\circ}$  and boiling at  $253^{\circ}$  to  $254^{\circ}$  (corr.), and is easily soluble in water, alcohol, ether, lignin, and hydrocarbons. It is oxidised into indigo by ozone, chromic acid, etc., and is hence of great importance for the synthesis of that colouring matter, also for that of certain odorifiers.

Its preparation from coal-tar oils is described in the Ger. P. 223304 of the Gesellschaft für Teerverwertung in Duisburg. From the above-mentioned fraction of the oils the phenols and strong bases of the aniline, pyridine, and quinoline series are removed by well-known methods, and the remaining oil is treated at temperatures between  $100^{\circ}$  and  $250^{\circ}$  with caustic potash, sodium, sodium amide, or sodium in presence of ammonia. The potassium-indol formed,  $C_8H_7NK$ , is mechanically removed from the remaining oil and decomposed by water. The indol is first obtained in the liquid form, but after the usual purification appears in the pure, crystallized state.

#### *Other Bases.*

G. C. Robinson and W. L. Goodwin (*Trans. Roy. Soc. Edin.*, 1878, p. 561, and 1879, p. 265) have obtained the following bases from the "vitriol tar" of Scotch shale-oil:—

Tetracoline,	$C_{12}H_{13}N$ ,	boiling at	$290^{\circ}$ to $295^{\circ}$
Pentacoline,	$C_{13}H_{16}N$ ,	"	$305^{\circ}$ " $310^{\circ}$
Hexacoline,	$C_{14}H_{17}N$ ,	"	$325^{\circ}$ " $330^{\circ}$
Heptacoline,	$C_{15}H_{19}N$ ,	"	$345^{\circ}$ " $350^{\circ}$
Octacoline,	$C_{16}H_{21}N$ ,	"	$360^{\circ}$ " $365^{\circ}$

Probably other bases of still higher boiling-points are also present in that tar.

#### *General Process for preparing the Bases from Coal-tar.*

Shake a sufficient quantity of coal-tar oils with a mixture of 1 part sulphuric acid and 2 parts water. Repeat this, if necessary. After standing for some time, draw off the clear liquid and boil it in an open vessel, or in a current of steam, until the mechanically present hydrocarbons have been driven off. (Pyrrol would go away as well, but Häussermann has shown that it must have been previously destroyed by the acid treatment.) Pass through linen cloth, add all excess of caustic soda solution, and distil. The steam carries over the bases;

if the distillate does not contain a sufficient quantity of these, saturate it with solid caustic potash (avoiding an undue rise of temperature) and decant the oily mixture of bases collecting at the top. If aniline is present, add cautiously fuming nitric acid and gradually heat up to boiling, whereby the aniline is destroyed. The other bases resist the acid; precipitate them by adding water, filter and saturate the filtrate again with caustic potash. The filtered oil still contains water which is removed by means of solid caustic potash. This must be done completely, because otherwise the boiling-points of the volatile bases are greatly altered, and the treatment with solid alkali must therefore be repeated several times. Now fractionate methodically; sometimes twenty fractionations are required before products of constant boiling-point are obtained.

Greville Williams destroys the aniline and its homologues by heating with potassium nitrite and hydrochloric acid; otherwise he proceeds as above.

According to a communication from Mr Häussermann, the preparation of bases with constant boiling-points is facilitated, at least for the compounds of lower boiling-points, by employing the crude hydrocarbons of the benzol series, which always contain bases. The 50 and 90 per cent. benzol of the British factories has been treated in them only with a small quantity of sulphuric acid, and always contains thiophenes and bases. From these benzols, after they have been fractionated in a Laval column into benzene, toluene, and xylene, up to 0.5 per cent. pure pyridine can be obtained (from the toluene) and 0.5 per cent. picoline (from the xylene). If this toluene and xylene is treated with dilute sulphuric acid, the bases are taken out and recovered at once in the pure state, since the single bases have been already separated by the fractionation on the large scale. Thiophen, thiotolene, and thioxene remain behind and can be extracted by concentrated sulphuric acid.

Instead of removing the aniline, etc., by means of nitric acid, or otherwise, Häussermann removes it in the form of sulphate, by treating the mixture of bases with dilute sulphuric acid as long as the difficultly soluble aniline sulphate is secreted, and obtains the other bases from the filtrate almost entirely free from aniline.

The quantity of bases contained in coal-tar is pretty consider-

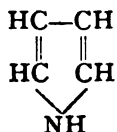
able. Since the pyridine bases have found an extended practical application for denaturing spirits of wine, they are recovered as a paying by-product in working up coal-tar. Kraemer has indicated a process of doing this on a large scale, and at the same time utilizing the waste sulphuric acid employed, which has been patented by the Chemische Fabrik Aktien Gesellschaft at Hamburg (Ger. Ps., 34947 and 36372, of 1885), and to which we shall revert in a subsequent chapter.

## B. NON-BASIC COMPOUNDS.

### *Pyrrol*, $C_4H_5N$ .

Discovered in coal-tar by Runge, isolated in the pure state from bone-oil by Anderson. Prepared by removing the basic oils by dilute sulphuric acid, and the nitrites by boiling with caustic potash, fractionating and converting the pyrrol contained in the fraction boiling from  $115^\circ$  to  $130^\circ$  into solid pyrrol-potash. In coal-tar it is contained only in small quantities, and difficult to extract from it.

Pyrrol is formed in various pyrogenetic reactions. It has been obtained by G. Williams (*Chem. News*, li., p. 15) by passing a mixture of acetylene and ammonia through a faintly glowing tube:  $2 C_2H_2 + NH_3 = C_4H_5N + H_2$ . Its structural formula has been established by Baeyer =



Hence it contains the nitrogen in the shape of an imide group. This has been experimentally confirmed by Lubawin (*Ber.*, ii., p. 99), and by the synthesis of pyrrol by Bell (*Ber.*, xiii., p. 877) and Bernthsen (*Ber.*, xiii., p. 1049) from succinimide by reduction. Hence the constitution of pyrrol is analogous to the furan and thiophen compounds, and according to V. Meyer (*Ber.*, xvi., p. 2974) it shows in fact the colour reactions with isatine, phenanthrenquinone, etc., characteristic for the thiophens.

Pyrrol is a colourless liquid of chloroform-like smell and burning taste; boils at  $133^\circ$ ; sp. gr. 1.077. Little soluble in

water, insoluble in alkalis, readily soluble in ether and alcohol, slowly in dilute acids. In the air it turns brown, but is again rendered colourless by distillation. It tinges a piece of resinous fir-wood moistened with hydrochloric acid, first pink, then crimson. It is indifferent towards most reagents, but is perhaps very slightly basic. No salts of it are known. With potash it forms a compound not decomposable by heat, but at once decomposed by water. With picric acid it forms a double compound from which, as found by Hooker (*Chem. Zentr.*, xci., p. 354), the pyrrol is already given off when drying it over sulphuric acid. Nascent oxygen forms hydropyrrols. By the action of chloroform upon potassium-pyrrol or an alcoholic solution of pyrrol and sodium alcholate, the five-carbon ring is converted into a six-carbon ring monochlorpyridine being formed.

When dry, gaseous hydrogen chloride is passed into an ethereal solution of pyrrol, it is polymerised into tripyrrol, which, on heating to  $300^{\circ}$  splits off ammonia and yields pyrrol and indol. The same reaction takes place with the homologues of pyrrol (Dennstedt and Voigtländer, *Ber.*, xxvii., p. 476).

#### *Methyl-Pyrrols*

have been synthetically produced; found also in bone-oil by Anderson, by Ciamician and Weidel (*Ber.*, xiii., p. 77), and by Dennstedt and Lehne (*Ber.*, 1899, pp. 1918, 1920, 1924), but not yet obtained from coal-tar.

#### *Cyanogen Compounds.*

We have already mentioned ammonium sulphocyanide; more about it in Part II. According to Vincent and Delachanal (*Comptes rend.*, lxxxvi., p. 340) tar contains also *methylic cyanide* (aceto-nitrile),  $\text{CH}_3-\text{C}\equiv\text{N}$ , which under the action of alkalis takes up the elements of water and yields acetic acid and ammonia. They found it in Paris benzol, together with carbon bisulphide, in that fraction of benzol which boils below  $80^{\circ}$ . This has been confirmed by Heusler (*Ber.*, 1885, p. 615).

Methylic cyanide boils at  $77^{\circ}$ ; sp. gr. 0.835. A colourless liquid of peculiar, not disagreeable smell, miscible with water in all proportions, and burning with a purple-bordered flame.



Similar compounds have been found in light coal-tar oils by Noetting (*Bull. Soc. Ind. Mulhouse*, 1884, p. 461), who considers them to be either methyl-isocyanide, boiling at  $59^{\circ}\cdot6$ , or ethyl-isocyanide, boiling at  $78^{\circ}\cdot1$ , and ascribes to them the poisonous action sometimes noticed with such light oils.

*Benzonitrile*,  $C_6H_5$ , CN,

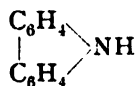
has been obtained from coal-tar by Kraemer and Spilker (*Ber.*, xxiii., p. 78), and is evidently the source of the benzoic acid found by K. E. Schulze (*Ber.*, 1897, Ref. p. 185) in the residues from the manufacture of carboic acid. It must be present in coal-tar in somewhat considerable quantities, as the manufacture of benzoic acid, derived from that nitrile, has been patented by the Aktien-Gesellschaft für Teer- und Erdöl-Industrie (Ger. P. 109122; Fr. P. 287934), which patent also describes the conversion of coal-tar benzo-nitrile into benzoic acid by saponification with caustic-soda solution of sp. gr. 1.4. Cf. Chapter IX., Degrez and Cambier (*Ber.*, 1896, Ref. p. 185).

It is a colourless liquid, smelling like oil of bitter almonds, boiling at  $191^{\circ}$ ; sp. gr. 1.023 at  $0^{\circ}$ .

*Carbazol*,  $C_{12}H_9N$ .

*Syn.* imidodiphenyl. Discovered by Graebe and Glaser (*Ann. Chem. Pharm.*, clxiii., p. 343; clxx., p. 88) in the residue from the purification of anthracene by caustic potash (Chapter VII.), in which a combination of it with potash, decomposable by water, is contained. It is always an important constituent of crude anthracene. Its properties are very similar to those of a hydrocarbon; like the hydrocarbons, it forms a compound with picric acid, fusing at  $182^{\circ}$  in large red prisms, which may be employed for preparing pure carbazol. The latter can also be purified by recrystallizing or subliming. It forms white scales or plates, insoluble in water, sparingly soluble in cold alcohol, ether, benzene, chloroform, more so at higher temperatures, and very soluble in pyridine; 100 parts of toluene dissolve at  $16^{\circ}\cdot5$  0.55, at  $100^{\circ}$  5.46 parts; 100 parts absolute alcohol at  $14^{\circ}$  0.92, at  $78^{\circ}$  3.88 parts. Fusing-point  $238^{\circ}$ ; it sublimes

readily and boils near  $355^{\circ}$ . It dissolves in pure cold sulphuric acid, the solution having a yellow colour; the most minute traces of nitric acid, chromic acid, chlorine, or other oxidizing agents produce an intense green colour. The chief characteristic reactions are: the red colour produced by HCl vapours on a firwood-splinter, soaked with the alcoholic solution of carbazol; the blue colour produced with isatin and sulphuric acid; and the crimson colour produced with a mixture of benzoquinone, acetic, and sulphuric acid. Water precipitates it unchanged from the cold solution in sulphuric acid; by heating, a sulphonc acid is formed. Nitric acid yields nitro-products. Carbazol is not changed by heating with soda-lime, caustic lime, zinc-dust, etc.; on heating with potash-lime a portion is decomposed, ammonia being formed. It has no basic properties, and forms no salts with acids, but a compound with acetyl and with potassium, in which the hydrogen of the imido-group is replaced by acetyl or potassium. It is the imido-compound of diphenyl:



as proved by its synthesis from aniline or diphenylamine by Graebe (*Ann. Chem. Pharm.*, clxvii., p. 125; clxxiv., p. 180). Several homologues and substituted carbazols have been synthetically produced.

A quantitative estimation of carbazol, according to Vaubel (*Z. angew. Chem.*, 1901, p. 784), can be made by titrating it in a solution in glacial acetic acid by means of bromine, each molecule of carbazol taking up 2 molecules of bromine.

Two isomeric *Dimethyl-carbazols* have been obtained, but not yet found in coal-tar. Homologous and substituted carbazols have been obtained by Täuber and Löwenherz (*Ber.*, 1891, pp. 1033 and 2597) from benzidine, tolidine, and their amides.

*Phenyl-p-naphthyl-carbazol*,  $\text{C}_{16}\text{H}_{11}\text{N}$ .

*Syn. imidophenylnaphthyl*. Discovered by Brunck in coal-tar, examined by Graebe and Knecht (*Ber.*, 1879, pp. 341, 2241), who obtained it also synthetically. Is obtained by subliming

the residue from distilling crude anthracene. Intensely yellow, but only by the admixture of some unknown substance; for on being fused with potassium hydrate it turns white. Almost insoluble in cold, very little soluble in boiling benzene or glacial acetic acid, more soluble in hot aniline. Toluene and absolute alcohol, when cold, dissolve next to nothing of it; boiling toluene dissolves 0.39 to 0.57, alcohol 0.25 per cent. The solutions have an intense blue fluorescence. It fuses at 330°, and has a higher boiling-point than sulphur. Its behaviour to sulphuric acid, etc., resembles that of carbazol.

The isomeric phenyl- $\alpha$ -naphthyl-carbazol (fusing-point 225°), and  $\beta$ -naphthyl-carbazol (fusing-point 170°) have only been synthetically obtained.

#### *Free Carbon (so-called)*

is found in every description of coal-tar, partly owing to coal-dust or coke-dust being mechanically carried out of the retort, but mostly by the decomposition of vapours on the hot sides of the retort, as proved by Köhler (*Z. angew. Chem.*, 1888, p. 577). Coke-oven tar contains much less free carbon than gas-tar (Kraemer, *J. Gasbeleucht.*, 1887). Speculations on the formation of free carbon in tar have been made by Bone and Jordan (*Chem. Zeit.*, 1901, p. 591).

It is mostly estimated by treating the tar with indifferent solvents, especially hot benzene, till nothing further is dissolved. The carbon found in German coal-tar by this method varies from 7 to 33 per cent.; tar containing much of it is not easily saleable, owing to the difficulty of distilling it down to hard pitch without injuring the stills. It is, however, certain that washing the tar or pitch with benzene, etc., does not yield really pure carbon, but only substances similar to anthracite or coke. Donath and Asriel (*Chem. Zentr.*, 1903, i., p. 1099) found in so-called free carbon 2.3 per cent. H., 3.7 N, 7.13 O, and only 89.2 per cent. real carbon.

Hodurek (*Oest. Chem. Zeit.*, vii., p. 365) found in Westphalian coke-tar on the average 4 per cent., but sometimes as little as 0.5 per cent. "free carbon," in gas-tar 20 to 25 per cent. His method for estimating the free carbon, to which we shall refer in a following chapter, yields less than that mentioned

above, and always yields a smaller percentage, but probably correctly so.

We come back to "free carbon" in Chapters V. and VI.

#### THEORY OF THE FORMATION OF THE CONSTITUENTS OF COAL-TAR.

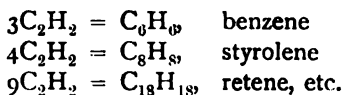
The fact that coal-tar contains principally aromatic substances was long ago explained by the assumption that coal is a mixture of compounds of the aromatic series, especially since Guignet (*Comptes rend.*, lxxxviii, p. 590) had proved the non-existence of really free carbon in tar. Baltzer (*Vierteljahrschr. d. Zürcher naturf. Ges.*, 1873) even went so far as to give hypothetical formulæ for various descriptions of coal. This, of course, only shows that coal may contain complicated compounds, from which the constituents of tar are formed by splitting-up.

E. Mills (*J. Soc. Chem. Ind.*, 1885, p. 325) holds that the process by which cellulose,  $nC_6H_{10}O_6$ , is turned into coal is essentially one of dehydration; so that, for instance, by heating wood to  $430^\circ$  without pressure, the residue has the composition  $nC_6H_2O$ ; and he assumes that in any case the organic matter in coal, shale, etc., corresponds to an initial symbol  $nC_6$  or  $2nC_3$ ; also that a definite relation exists between the C of the fixed carbon on the one hand and the C of the gas + tar on the other, in which  $C_3$  is always the fundamental unit. We must refer for details to the original, merely pointing out two oversights in that reasoning (which, of course, were quite well known to the author), namely, that woody fibre is not at all  $=nC_6H_{10}O_6$ , the formation of oxycellulose, lignin, etc., having intervened, and that the formation of coal from woody fibre is anything but a mere dehydrating process,  $-CO_2$ ,  $CO$ ,  $CH_4$ , and other carbon compounds being liberated at the same time as water. (The paper of Mills has been very adversely criticised by Dittmar, *Chem. Ind.*, 1891, p. 512).

Berthelot has, in a number of papers published in the *Ann. Chim. Phys.*, in 1866, 1867, 1869, and 1877, formulated a complete theory of the building-up and the splitting-up of compounds by pyrogenetic reactions. Complex compounds are formed.

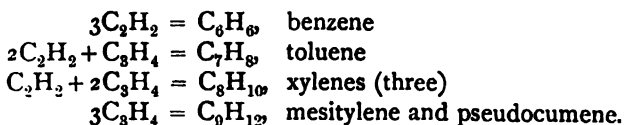
which are decomposed into simpler ones, and these unite again to form higher compounds, thus producing a very complicated equilibrium among a large number of hydrocarbons. Hydrogen largely enters into this series of reactions, both by being split off and by being added to other compounds.

Acetylene seems to play a very important part in the formation of the substances composing coal-tar. According to Berthelot (*Comptes rend.*, lxii., pp. 905, 947), on heating acetylene over mercury in a bent glass tube up to the softening-point (*i.e.*, to a dark red) there was produced, together with a number of secondary products occurring in small quantity, a large amount of benzene, styrolene, naphthalene, retene, etc. At a bright red heat another kind of decomposition set in; then acetylene was almost completely split up into its elements. Berthelot consequently regards benzene as triacetylene, styrolene as tetracetylene, retene as enneacetylene: thus,



The aliphatic substances likewise yield acetylene under the action of heat; and Berthelot ascribes the formation of aromatic compounds, always observed in this case, to the secondary condensation of acetylene by itself and with other compounds.

Similar conclusions are arrived at by O. Jacobsen (*Ber.*, 1877, p. 853) who, besides acetylene, assumes its next homologue, allylene,  $\text{C}_3\text{H}_4$ , to participate in the synthesis. This is shown by the following equations:



This hypothesis would explain why,

1st, besides benzene, only those homologues occur the lateral chains of which consist of methyl;<sup>1</sup>

<sup>1</sup> Jacobsen himself has had to modify this part of his theory. In the *Ber.*, 1886, p. 2515, he declares it to be proved that coal-tar contains benzene substitution-products with longer lateral chains, but he was not able to obtain these in sufficient quantity to identify them.

2nd, the methylbenzenes found in tar-oil do not extend beyond the tri-derivatives ;

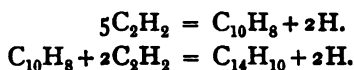
3rd, of all possible tri-derivatives only mesitylene and pseudocumene are present ;

4th, all three xylenes occur in tar-oil.

(The last is made clear by the graphic reaction schemes given in the original.)

Allylene has not yet been observed among the products of destructive distillation ; but Jacobsen ascribes this to its easier condensation, and to the difficulty of discovering small quantities of it mixed with acetylene.

Even on Jacobsen's theory the formation of the other hydrocarbons occurring in tar can only be explained by elimination of hydrogen, as shown by Anschütz (*Ber.*, 1878, p. 1215).



Anthracene and phenanthrene might also be formed by a condensation of ditoluene :



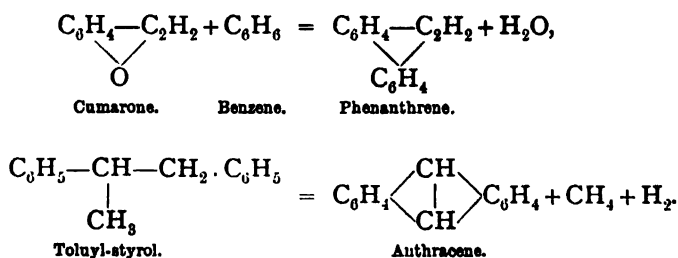
It is an argument in favour of Jacobsen's theory that coal-tar has certainly been found to contain only methylated benzene homologues, exactly those mentioned by him, but neither cumene (isopropylbenzene), nor propylbenzene, nor ethylmethylbenzene. It is true that older treatises enumerate cymene (methyl-isopropylbenzene) as a constituent of tar, but upon insufficient evidence ; so that nowadays cymene is not considered to be present in tar. But since K. E. Schulze has discovered tetramethylbenzene in coal-tar, Jacobsen's theory can no longer be upheld without some modification. K. E. Schulze himself (*Ann. Chem. Pharm.*, ccxxvii., p. 143) has originated another theory as to the formation of the hydrocarbons found in coal-tar. He believes the phenols to be the primary products, and the hydrocarbons to be formed from them by the splitting-off of the elements of water. This theory has obtained some support from the investigations of Kraemer (*Annalen*, clxxxix., p. 129) ; Köhler (*Ber.*, 1885, p. 859) ; and Staveley (*Chem. Zeit.*, 1889, p. 1108) ; Watson Smith (*J. Soc. Chem. Ind.*, 1883, p. 495),

on the other hand, cites observations militating against at least its general application.

The hypothesis that acetylene is the principal factor in the formation of the coal-tar hydrocarbons does not harmonize very well with the researches of Vivian B. Lewes on the formation and behaviour of acetylene (*Chem. Zeit.*, 1892, p. 384), according to which acetylene is formed only at the highest temperatures; while Bunte has proved (*J. Gasbeleucht.*, 1886, p. 595) that most of the tar is formed during the first hour of the distillation of coal—that is, at a comparatively low heat. According to Heintz (*ibid.*, 1886, p. 294) the temperature of the gas-retort during the first hour averages 420°, after 3 hours 960°, and after 5½ hours 1075° C.

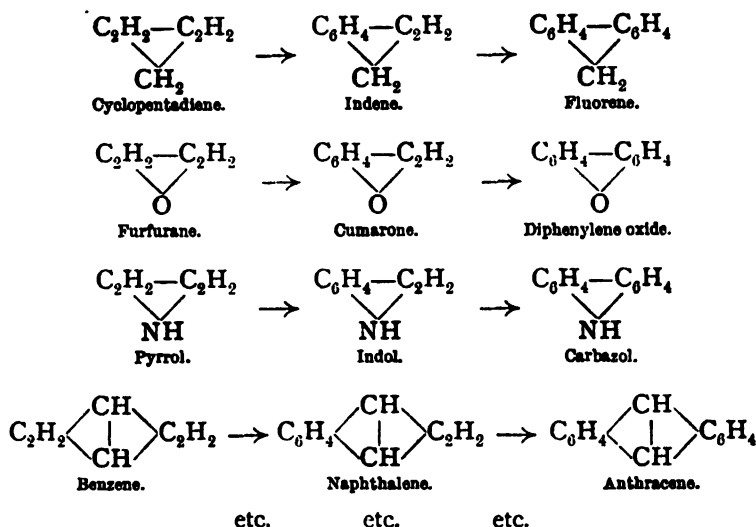
Haber (*Ber.*, 1896, p. 2691) discusses the part played by acetylene in the formation of benzene and other hydrocarbons. Heusler (*Ber.*, 1896, p. 2773) believes that benzene and its congeners are mostly primary products of the dry distillation of coal; he was led to this conclusion principally by his study of the behaviour of lignite and lignite-tar.

Kraemer and his co-operators, Spilker, Eberhardt, and Klotz (*Ber.*, 1890, pp. 84, 3169, 3268, 3276), have adduced important objections against the theory that the *higher* aromatic hydrocarbons are formed from acetylene, and in support of the theory that they are formed from cumarone and styrol by condensing with the lower hydrocarbons, *e.g.* :



They believe (*ibid.*, 1896, p. 552) that the pyrogenetic products are principally formed from the original products of decomposition (methane, ethylene, acetylene, formaldehyde, and ammonia), by polymerization and condensation with expulsion of hydrogen. As the process continues one or more

acetylene groups are replaced by phenylene groups, and thus we obtain the following series:—



Probably none of the above-mentioned hypotheses can claim general application, and possibly all those reactions are concurrently at work in the formation of the exceedingly numerous constituents of coal-tar.

K. E. Schulze observed (*Ber.*, 1887, p. 409) that most of the tar substances belong to the *meta*-compounds, which are more stable than *ortho*- and *para*-compounds.

Russig (*Z. angew. Chem.*, 1899, pp. 948, 951) makes various objections to the theories of Berthelot, Jacobsen, and Kraemer, and develops a theory of his own, according to which the formation of coal-tar must be explained by the constitution of coal itself, and by the decomposition of the complicated cellulose molecules existing therein.

Vivian B. Lewes (*ibid.*, p. 826) points out that tarry matters are sometimes formed during the generation of acetylene from calcium carbide, and benzol can be proved to exist in the scrubbing liquids, which facts point to the formation of aromatic hydrocarbons by polymerization of acetylene.

Further papers on this subject are by Semmler (*Ber.*, 1891, p. 204); Weger (*Z. angew. Chem.*, 1909, p. 338); K. E. Schulze



(*Annalen*, ccxxvii, p. 143); Kramers (*ibid.*, clxxxix, p. 129); Köhler (*Ber.*, 1885, p. 859); Staveley (*Chem. Zeit.*, 1889, p. 1108); E. von Boyen (*Chem. Zeit.*, 1889, p. 905); Ipatieff (*Chem. Zeit.*, i., p. 360); W. von Bolton (*Z. Elektrochem.*, 1902, p. 866).

## APPENDIX

### *Poisonous Property of Coal-tar.*

It is hardly necessary to say that coal-tar has strongly poisonous properties when it gets into the human body. But even its action on the skin is decidedly injurious, and leads to bad skin-diseases which are sometimes confused with the "acne," a sort of itch, occurring at electrolytic chlorine-works (where very much tar is used for protecting the apparatus). Russig, in *Chem. Ind.*, 1902, pp. 238, 432, has drawn attention to this. It is also treated by Rambousek in a paper on injurious gases in industrial work (*Z. Gewerbehygiene*, Vienna, Vol. IX.). At paraffin works it is called "paraffin itch," and seems to be identical with the chimney-sweeps' cancer, several times mentioned in the English factory inspectors' reports. Especially in the manufacture of pure anthracene this troublesome disease has been frequently noticed, but by insisting on cleanliness on the part of the workmen it may be avoided altogether.

We shall treat of "pitch cancer" in Chapter VI.

Gräf (*Prometheus*, 1914, p. 124) reports on chronic poisoning by benzol vapours; also, on morbid phenomena caused by coal-tar pitch in consequence of photodynamic action; and on tumours in the urethra in the case of men employed in the manufacture and use of aniline colours.

## CHAPTER IV

### THE APPLICATIONS OF COAL-TAR WITHOUT DISTILLATION

As we have seen on pp. 18 *et seq.*, considerable time elapsed after the successful introduction of gas-lighting before means could be devised for disposing of the tar obtained during the manufacture of the gas, or at least before it was regarded as a source of profit. Probably at that time the tar was burnt as much as possible, under the gas-retorts, but this is not quite as easy as it might appear (see below), and only more recently the application of tar as fuel has been improved. Coal-tar was no doubt also employed from the first as a cheap paint for wood and metals, although it is but little adapted for that purpose in the raw state. Some more was used for the manufacture of soot, and of roofing-felt. But this would account for only a portion of the coal-tar obtained, and most of it remained a great nuisance to the gas-manufacturers, who had sometimes to pay considerable sums to get rid of it. This, no doubt, led to the first attempts at utilizing the tar by distillation, which we shall mention in Chapter V.

Before, however, gas-tar was distilled on a manufacturing scale in order to isolate the valuable substances contained in it, of course it had to be employed in other ways, either in the raw state or thickened by evaporation. Even later on the tar could not, and in some places up to this day cannot, be distilled to advantage, principally owing to the cost of carriage; and it was necessary to find other uses for it, in order to get rid of it.

Recently, as we have seen above (p. 26), the great fall in the prices of coal-tar products has led to such a depreciation of coal-tar itself that the question of disposing of it in other ways than by distillation has become much more urgent than before.

We shall in this chapter describe such applications of coal-tar as are made without submitting it to a proper distillation,

consequently either in the entirely raw state or merely deprived of water (and necessarily at the same time of its most volatile constituents) by preliminary heating.

*Application of Coal-tar to the Manufacture of Illuminating-gas.*

This can be effected by passing the tar through red-hot tubes, or by heating it in a still and treating the vapours evolved in the manner just mentioned. This was the intention of the process of Koechlin, Duchatel, and Perpigna,<sup>1</sup> that of A. Bernard<sup>2</sup> (who ran the tar upon the coke remaining in the gas-retorts), that of Droinet<sup>3</sup> (who moulded the tar, mixed with ashes, coal-dust, sawdust, clay, etc., into compact lumps which were heated in ordinary gas-retorts), and that of Isoard<sup>4</sup> (whose tar-gas, prepared by superheated steam, contained, according to Monier's analysis, 17.8 per cent. ethylene and 71.9 per cent. "light hydrocarbon," *i.e.*, methane—which seems very doubtful). Similar processes are indicated in the B. Ps. of Hengst, Watson, Muschamp, and Wilson (1858), and that of MacCracken, Newton, Kirkland, and Husson. Still and Lane (B. P. 6th October 1871) mixed tar, together with some vegetable matters with gas-coal. According to Bunte<sup>5</sup> all these endeavours could not but fail, as those substances which, by decomposing at a high temperature, furnish permanent gases are present in coal-tar in too small a quantity. Nevertheless fresh attempts will be made in this direction now that tar is of so little value. It is true that raw tar seems very badly adapted to gas-making, since the pitch, which forms the greater part of its bulk, is almost devoid of light-giving substances, and since, moreover, the pipes are very easily stopped up in the operation; but it is possible that tar deprived of its pitch, naphthalene, and anthracene, as proposed by G. E. Davis, would be a suitable material for the above purpose. Even this is contested by L. Wright, as we shall see at the close of the next chapter.

Bäcker,<sup>6</sup> who had obtained a Ger. P. No. 43096, for a process of mixing tar with coke-dust and introducing this mixture in small portions into a red-hot gas-retort, claims to

<sup>1</sup> B. P. of 1854.

<sup>2</sup> *Dingl. polyt. J.*, cxlviii., p. 292.

<sup>3</sup> *Ibid.*, cxlviii., p. 295.

<sup>4</sup> *Ibid.*, clv., p. 462.

<sup>5</sup> *Schilling's Gasbeleucht.*, 3rd ed., p. 231.

<sup>6</sup> *J. Gasbeleucht.*, 1887, p. 908; *Z. angew. Chem.*, 1889, p. 16.

have obtained excellent results, but Bunte (*J. Gasbeleucht.*, 1887, p. 105) most distinctly contradicts this.

Ellery,<sup>1</sup> who worked with an inclined cast-iron retort, obtained from a ton of tar upwards of 15,000 cub. ft. of 15-candle gas, apart from coke and ammonia.

Hempel<sup>2</sup> proposed working up gas-tar in a Lowe's or Granger's water-gas plant.

Burns<sup>3</sup> distils tar, while blowing in steam, to dryness; the gases are made to enter into a heated chamber, where they are well mixed and then pass through red-hot pipes filled with charcoal, where they are decomposed into illuminating-gas. According to the quantity of steam, the gas turns out either of greater illuminating-power or of greater heating-power. One gallon of tar and 2 gall. of water furnish 700 cub. ft. of 16-candle gas. When distilling coal at low temperatures and treating the tar as above, 1 ton of coal is stated to furnish 21,000 cub. ft. of gas (?).

Merkens<sup>4</sup> injects a spray of tar produced by a steam-injector into retorts half filled with coke. John Smith<sup>5</sup> describes another process for turning tar into gas.

Grebel<sup>6</sup> made experiments on the production of gas from tar mixed with coke or sawdust. One hundred kg. tar with 100 kg. sawdust and 20 kg. coke yielded 76 cbm. gas, 55 of which must be attributed to the sawdust. One hundred kg. tar and 250 kg. coke-dust yielded only 21 cbm. gas. In order to produce the illuminating-power of one candle, we require 42.9 litres of the first, and 31.4 litres of the second gas, as compared with 10.4 litres ordinary coal-gas. Those tar-gases therefore possess only 25 to 33 per cent. of the illuminating-power of coal-gas. Leybold's experiments on the same subject<sup>7</sup> were equally unfavourable.

Much stir was produced at one time by the Dinsmore process (B. P. No. 7714, 1887 (amended 24th May 1890); No. 15852, 1887; No. 4885, 1888; No. 2096, 1888; No. 16194, 1888), on which Carr<sup>8</sup> and Watson Smith<sup>9</sup> have made reports. Its principal feature is: passing the crude coal-gas, inclusive of tar

<sup>1</sup> *J. Gasbeleucht.*, 1895, p. 117.

<sup>2</sup> *Ibid.*, 1887, p. 521.

<sup>3</sup> B. P. No. 14958, 1886; *Iron*, 1887, p. 521.

<sup>4</sup> *J. Gasbeleucht.*, 1891, p. 188.

<sup>5</sup> B. P. No. 7605, 1893.

<sup>6</sup> *Dingl. polyt. J.*, cclxvii., p. 32.

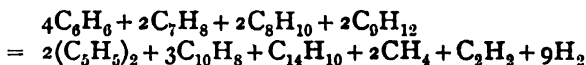
<sup>7</sup> *Ibid.*, cclxvii., p. 32.

<sup>8</sup> *J. Soc. Chem. Ind.*, 1889, p. 960.

<sup>9</sup> *Ibid.*, 1890, p. 446.

and ammonia, from the gas-retorts into another retort heated by the same fire, and thus gasifying the tar by superheating. The volume of the gas is stated to be increased 10 per cent. and the illuminating-power to rise from 15 to 20 or 21 candles.

Kraemer's experiments<sup>1</sup> with the Dinsmore process led to a very unfavourable result. He found that the increase of volume of the gas is caused entirely by the decomposition of the methane and the olefines, the gas becoming much poorer in these and richer in naphthalene and phenanthrene. The decomposition of the benzenoid substances in the tar may be represented in the most favourable case as follows:—



leaving the extensive separation of free carbon out of consideration. In 100 kg. of tar only 2.5 kg. benzenoid substances are contained, which, if decomposed as above, would account for an increase of 0.66 per cent. of the volume of the gas. The increase would rise to 1 per cent. if the phenols were decomposed in the same manner. Naphthalene is hardly changed; the heavy oils are also very persistent against heat, and at most split off a little hydrogen and methane. The pitch and soot contained in the tar have no action whatever. Hence the Dinsmore process effects nothing else than a hot distillation of the coal, viz., increased production of gas, diminished illuminating-power, obstructions by tar in the rising main and by naphthalene in the gas-pipes.

Exactly the same negative results have been obtained by the Deutsche Continental Gas-Gesellschaft<sup>2</sup> with the Dinsmore process.

Watson Smith (cited above) compared the composition of tar, obtained from the same coal by the Dinsmore process and by the ordinary process, with the following result:—

	Dinsmore Tar.	Ordinary Tar.	per cent.
Water . . .	1.1	7.1	
Light oil . . .	1.3	5.4	"
Creosote oil . . .	16.5	17.8	"
Anthracene oil . . .	12.1	8.6	"
Pitch . . .	69.0	61.0	"
Sp. gr. of tar . . .	1.157	1.150	"

<sup>1</sup> *J. Gasbeleucht.*, 1891, p. 225; *Fischer's Jahresber.*, 1891, p. 47.

<sup>2</sup> Priv. comm., by Dr Bueb, Dessau.

The creosote oil (containing about 50 per cent. naphthalene) showed :—

Sp. gr. . . . .	1.030	1.025	
Crude carbolic acid	2.5	5.7	per cent.
Anthracene (pure) .	0.79	0.32	„

Hence there is no improvement in the quality of tar ; any increase of the anthracene is more than made up by loss of benzol.

Rincker and Wolter (Fr. P. 391868, 1908) introduce tar into a red-hot gas-producer. The gas formed here is partly carried away by its own pressure ; the remaining tar vapour is forced by a current of air into a second producer and is there

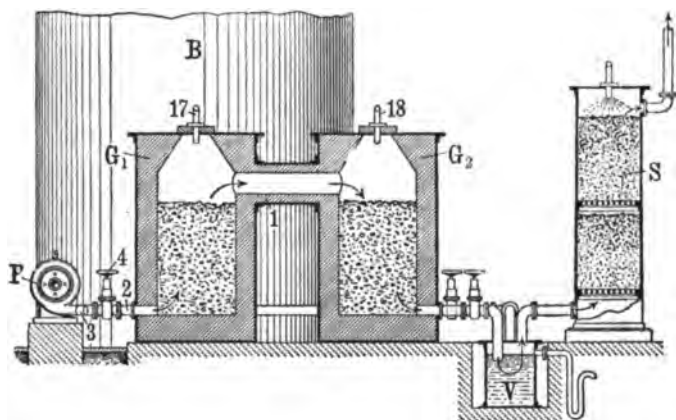


FIG. 30.

converted into a permanent gas. At the same time a blast of air brings up the first producer to a red heat, and the process is reversed by introducing tar into the second producer.

This process, patented in Germany as No. 239343, 1909, is carried out by the Berlin-Anhaltische Maschinenbau-Aktiengesellschaft as follows. The gas is made in a double producer, Fig. 30, in which the oil- or tar-vapour, remaining after the de-gasifying process, are passed in turns from one producer through the charge of the other producer. Both producers,  $G_1$  and  $G_2$ , are worked with hot air, blown in turns from one to the other ; that producer being always connected with the service-pipe which has first received the blast. The gas spaces of  $G_1$

and  $G_2$  are continuously connected by flue 1. At the bottom we see the air-conduits 2 and 3, which can be closed by valves 4. The blast is produced by a centrifugal, F. V and S are a receiver and scrubber for purifying the gas. The generators are filled with coke up to the connecting-flue 1; through pipes 17 and 18 they receive the oil or tar to be gasified. The receiver, V, consists of three wrought-iron boxes, into which the gas-pipes from the producers are dipping; this arrangement serves both for shutting off the producers against the other parts of the apparatus, and for retaining any coarse impurities. The purifying apparatus now following is just like that found in all gas-works, comprising a cooler, a scrubber, and two bog-iron ore purifiers. The work is carried out as follows. The hot air is blown through pipe 2 into the bottom of one of the producers, passes at the top through the flue 1 into the other producer, and away from this at the bottom, traversing the purifying plant. Now the oil or tar is pumped through tuyeres on to the red-hot coke, and while passing through this from the top downward is transformed into permanent gas which now, together with the producer-gas, enters into another chamber of the receiver where the soot is washed out by flowing water. Of the 80 to 85 per cent. carbon contained in the tar or oil, only a very small portion is found in the gas in the shape of hydrocarbons or carbon monoxide; by far the greatest portion remains attached to the coke in the producers, where it is burned during the hot-blast period, and thus economises coke. The two producers serve in turns for gasifying and hot-blowing. The tar used in this process may be coal-tar, water-gas tar, oil-gas tar, lignite-tar, or any other tar. When using coal-tar (gas-tar) the gas passing away has a heating-value of 4200 to 4500 calories, a specific gravity of 0.44 to 0.47; its composition is:—

						Per cent.
$CO_2$	.	.	.	.	.	1.0
$C_nH_{2n}$	.	.	.	.	.	2 to 4
O	.	.	.	.	.	0.6 „ 1
CO	.	.	.	.	.	12 „ 15
$CH_4$	.	.	.	.	.	10 „ 12
H	.	.	.	.	.	55 „ 62
N	.	.	.	.	.	8 „ 11

The consumption of raw materials for 1 cbm. of tar-gas is about 2 kg. tar and 300 g. coke. The tar must be warmed

up and, if necessary, filtered, in order to be sufficiently thin-flowing. By changing the style of work without any change of the plant, very light gas, even nearly pure hydrogen, can be made for aerial navigation.

A plant for enriching water-gas by the products of the destructive distillation of coal-tar has been erected at Hythe, in the county of Kent (*J. Gasbeleucht.*, 1908, p. 110). The gas-producer contains a layer of coke, 4 ft. 8 in. deep, and is worked by draught, produced by a water-cooled steam-jet exhaustor in the outlet chimney. The tar is introduced in the hottest part of the producer by two opposite tuyeres, placed underneath a small arch, so as to create a very hot free space. It is injected under a pressure of 0.4 atmosphere, by turns on opposite sides, 1.3 gall. of tar to 1000 cub. ft. of gas. The gas is enriched by benzol, injected from above by means of a pump, using 2½ lb. to each 1000 cub. ft. One man can serve two such producers.

At Detmold, according to *J. Gasbeleucht.*, 1910, p. 109, experiments were made on gasifying tar. At first the tar was introduced into the gas-retort at the end of the working of a charge, but this did not produce good results. The formation of graphite at the retort-walls was increased, the coke was covered by a glassy, badly combustible crust of tar graphite, and the starting and stopping required special attention. It was then tried to gasify the tar in a continuous way by running it into an empty retort. Hereby at lower temperatures crusts of graphitoid hard pitch, and at higher temperatures numerous flakes of graphite on the retort cover were formed, but this did not take place when steam was blown in. The experiments were interrupted on account of frequent stoppings of the supply of tar, but they were to be resumed later on with steam-jet atomisers.

Bunte (*ibid.*, 1910, p. 777), on account of experiments made by himself, has very slight hopes of success for gasifying the tar within the retort. The tar contains only a very small proportion of coal particles which have escaped gasification; it consists mostly of pyrogenetic products, formed at high temperatures. The former would yield a little gas, but the latter could only be decomposed at temperatures higher than those at which they have been formed. Practical experiments show that only a small portion of the tar can be converted into gas. Bunte for his experiments employed dehydrated



tar, and soaked it up in completely degasified coke-breeze. During several days he gasified a mixture of 1 ton of tar + 2 tons of coke-breeze at the comparatively low temperature of about  $1050^{\circ}$ , with the following results. One hundred kg. tar, worth about 1s. 7d., yielded 30 cbm. of gas, that is about the same quantity as would be obtained from 100 kg. coal of approximately the same price. But the tar furnishes no valuable by-products, so that the gas would be made much more cheaply from coal. Moreover, the heating-value of the tar-gas was only about 4500 calories. Therefore from 100 kg. of tar, possessing a heating-value of about 880,000 calories, we obtain in the gas 135,000 calories, that is 15 per cent. or hardly 1 per cent. of the heating-value of the coal from which the tar has been derived. The increase of the weight of 100 kg. tar was only 62.7 kg.; the coke, therefore, contained 500,000 calories = 57 per cent. of the heating-value of the tar. In the end the coke-breeze was only quite loosely coherent, and certainly not more easily applied or saleable than the original breeze. A specially important fact is that 20 per cent. of the tar passed over into the receiver and the service-pipes, and saturated these with a substance resembling cart-grease. Hence it is impossible to attain a technically practicable and economical gasification of the tar. Bunte, however, considers it possible that better results might be obtained when using tar in a water-gas producer, or by heating it by means of superheated steam to the temperature of the water-gas process.

Wyatt (*Gas World*, 1915, lxii, p. 756) describes the gasification of tar as carried out in practice.

### *Burning Tar as Fuel.*

Where all other employments fail to procure a satisfactory outlet for the tar, it must be burned; and this is mostly done under the gas-retorts themselves. Its heating-value is, in this case, stated to be one and a half, or even twice that of coke; but this is exaggerated, as we shall see below. This employment of tar has always been the only practicable one where the distance of the gas-works from tar-distillers was too great and other uses of tar were too scanty; and during the last great fall of prices the burning of tar as fuel for the retorts has come

to the fore again, even in some of the manufacturing centres, where such a process a few years ago would have been thought a ridiculous waste. In 1901 Russig (*Chem. Zeit.*, 1901, p. 90) stated the fact that at that time thousands of truckloads of tar were burnt, either in the raw state, or merely freed from water, ammonia, and the lightest oils by settling out or by a preliminary heating.

The simplest way of burning tar is by mixing some of it with coke. W. Bäcker (*J. Gasbeleucht.*, xxix., p. 338) runs tar into the fireplace, about 16 in. below the surface of the coke, and finds that he can thus burn about 1 lb. of tar to 4 lb. of coke. This is also the plan most usually adopted at English gas-works; but it appears that much less tar is burned here in proportion to the coke. Mr Trewby states the quantity of tar used at the Beckton works = 5 gall. per ton of coke (*J. Soc. Chem. Ind.*, 1886, p. 563). Mr Wright (*ibid.*) also considers this to be the best way of burning the tar.

We shall describe some of the most suitable arrangements for burning tar, which equally apply to any liquid or easily liquefiable products of the distillation of tar for which no other outlet can be found (as is occasionally the case with some descriptions of "heavy" or "dead" oil, *cf.* Chapter VIII.), also to petroleum-residues and the like. We therefore take our descriptions partly from such places where as yet no tar, but petroleum-residues are burned, as they may be useful for tar as well.

That this subject has recently become of greater importance than previously is best shown by the large number of new patents taken out during the last few years; but we shall more particularly enter upon the description of apparatus seen working on the spot by competent observers.

So long ago as 1862,<sup>1</sup> patents were taken out in the United States by Bidley, by Shaw, and by Linton, for the use of liquid fuel; in 1864 an apparatus, by Richardson, was tried at Woolwich. Aydon and Shpakovsky, in 1865, devised arrangements for injecting the fuel as a spray, the former using steam, the latter a blast of air. Watson Smith used steam to inject creosote oil for boiler fires about 1867. In 1867, at the request of Napoleon III., H. St. Claire Deville constructed an apparatus, which, however, proved a failure on being put to a practical test

<sup>1</sup> Redwood, *J. Soc. Chem. Ind.*, 1885, p. 78.

in Russia. Audouin, in 1869, invented a more suitable burner. Other more successful burners, which are now being used in Southern Russia, date from 1870 and later.

The simple plan of dropping tar into a hot fireplace is unsatisfactory; the combustion is very incomplete, and the consequence is that clouds of dense black smoke are sent forth

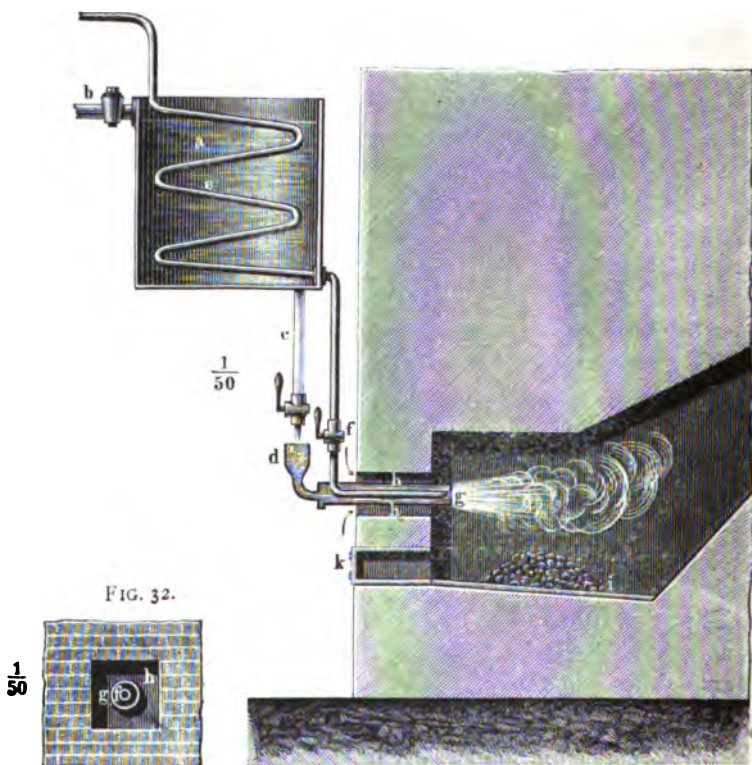


FIG. 31.

(such as are seen hanging over the primitive Tatar distilleries at Baku), along with a very disagreeable smell of partially-burnt tar or petroleum. Hence special means must be employed to prevent these drawbacks. We shall enumerate, in the following, only the more important of the very many different descriptions of apparatus invented for this purpose.

An arrangement for burning tar, which answers its purpose fairly well is shown in Figs. 31 and 32: *a* is an iron tank for tar

(creosote oil, etc.) which runs in from a tap (*b*), best constructed as an automatically-acting ballcock, so that the level shall remain always the same, and the tar run off in a uniform stream through the pipe and out of the tap *c*, in an open jet (so that any choking-up can at once be observed) into the funnel *d*, and from this into a horizontal iron tube (*g*) which ends inside the fireplace. In the centre of the tar-pipe is a steam-pipe (*f*), which first passes as a worm (*e*) through the tar-tank *a*, and keeps it always warm. A tap (*f*) permits the regulation of the steam-jet, which, as it issues in the centre of the extremity of the tar-tube, converts the tar into a fine spray, and at the same time, acting as an injector, carries in through the open space *h*, which surmounts the pipe *g*, the air necessary for combustion. Thus the tar is brought into very intimate contact with air, and is almost instantaneously burned; a little of it falls down upon the plate *i*, where it burns into coke, which is removed from time to time through *k*.

Fig. 33 shows a contrivance for burning the tar without a steam-jet, by Liegel,<sup>1</sup> specially intended for heating gas-retorts by tar. The tar drops through an opening (*a*) 1½ in. wide, upon a plate (*b*) 5 ft. 3 in. below, which reaches through the front wall and is shut off by the door *c*. The latter consists of a slide, moving air-tight on its bed by means of a screw. The air for combustion enters below the slide, and first meets a bed of red-hot tar-coke, collecting on *b*, which it burns into light-grey ashes. The tar is partly burned by the radiated heat of the fireplace; but most of it falls on to the tar-coke burning below, is spread out, and meets the air coming in from the door-slide. The small door, *c*, is opened every half-hour for loosening the coke and getting out the ashes. Another door (*d*), with a peep-hole, is placed higher up, and is likewise to be closed air-tight.

Schilling (*ibid.*, p. 324) also figures a special "squirting-cock" for the tar, shown in Fig. 34. The vertical branch *a* is screwed upon the tar-supply pipe. The end turned towards the furnace is closed by a cap (*b*) with an opening about  $\frac{1}{8}$  in. wide. The other horizontal end (*c*) is provided with a gland through which passes a long screw (*d*), which carries a horizontal needle (*e*). The outer end of *e* is provided with a small wheel (*f*), and

<sup>1</sup> From Schilling's *Gasbeleuchtung*, 3rd ed., p. 325.

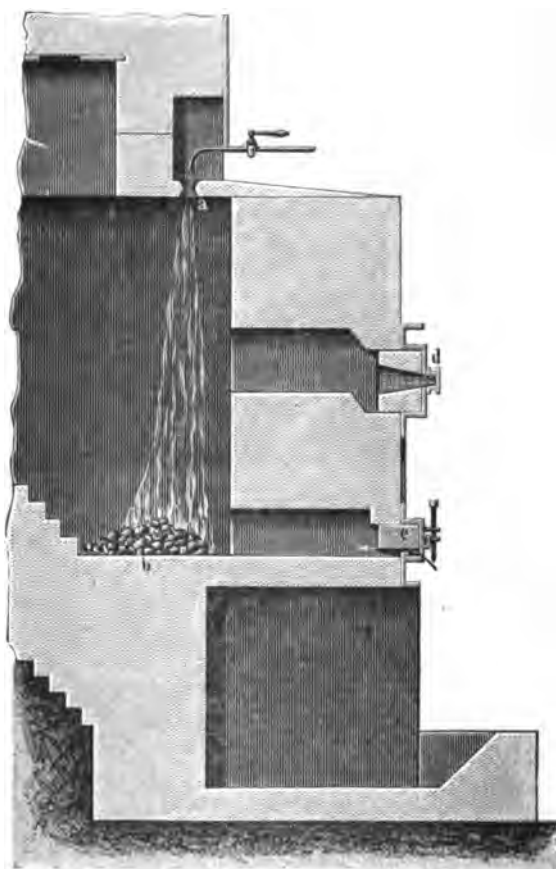


FIG. 33.

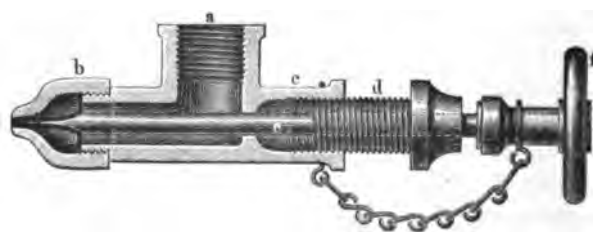


FIG. 34.

is fixed by a small chain. The needle (*e*) serves for partly or entirely closing the opening (that is, for regulating the jet of tar), also for cleaning it out in case of need. The apparatus is fixed in the furnace-front, so that a slide can be put in front of it. In the case of gas-retorts there ought to be on the fireplace-bed a 4-in. layer of red-hot coke, which is broken up every half- or three-quarters of an hour. This bed ought always to be dry; otherwise too much tar has been run in, or too little air has been admitted. For the purpose of making a start, a small wood-fire is made on the hearth and the tar is run in at once.

H. T. Litchfield and D. Renshaw (Ger. P. 17659, 1881) have constructed a special kind of nozzle for blowing in a mixture of the combustible liquid with air and steam, in such a way that a converging whirl is caused which intimately mixes the liquid with the air.

Another mixing-apparatus, evidently intended more for petroleum, has been patented by the Boston Petroleum Heating Company (Ger. P. 21648, 1882).

O. D. Orvis<sup>1</sup> (Ger. P. 28017; in England patented as a communication to A. T. Boulton, No. 5357, 1883) describes an apparatus, the essential novelty of which is a retort fixed to the inner end of the inlet pipe, in which any less volatile portion of the oil blown in may collect and may be vaporized by the fire; also a horizontal nozzle through which the mixed stream of steam, hydrocarbon, and air may issue in a sheet-like form.

R. B. Avery (B. P. 5795, 1883) fits the oil-supply pipe with a series of perforated diaphragms of gradually decreasing mesh, in order to "atomize" the oil before it enters the steam-pipe.

J. H. Selwyn (B. P. 2160, 1884) burns liquid hydrocarbons in conjunction with water-gas or steam in presence of a substance containing both carbon and iron, preferably employing plumbago, in a furnace specially described.

J. Leede and G. H. Ouray (B. P. 1864, 1884, a communication to W. P. Thompson) mix the liquid hydrocarbons with

<sup>1</sup> This and a number of other apparatus are described and figured in *Dingl. polyt. J.*, vol. cclviii, p. 418, and in Wagner-Fischer's *Jahresber. d. chem. Techn.* for 1885, pp. 313-1318.

earthy matter, and describe special apparatus for feeding, igniting, and consuming that kind of artificial fuel.

J. D. Bodwell (B. P. 7615, 1885) employs a closed chamber fitted with shelves, sloping downward from the sides; the oil or tar falls from shelf to shelf, burning during its passage (*cf.* Nobel's shelf-burner, later on).

H. de Bray and C. D. Rosetti (B. P. 12990, 1885, a communication to J. Imray) fix to the crown of the fire-flue of an ordinary Cornish boiler a retort, into which oil or tar is admitted; a pipe leads the oil or gases to a receptacle on the fire-bars, to which a supply of air under pressure is also admitted.

A somewhat similar apparatus has been patented by P. Tarbutt (B. P. 5599, 1886).

J. Buffett (Ger. P. 30995, 1884) uses the steam first for heating up the oil, before it serves for converting it into a spray.

E. C. Burgess (Ger. P. 29614, 1884) avoids the use of a steam boiler by generating the steam, required for producing the spray, from liquid water, by means of a worm and retort fixed within the fire-box.

J. B. Archer (B. P. 6347, 1886) patents an apparatus for firing steam-boilers by means of liquid hydrocarbons which are not "atomized," but are previously gasified.

William de St Martin (Ger. P. 36134) decomposes mineral oils along with steam in a red-hot retort, and mixes the resulting gases by means of an Archimedean screw previous to burning them.

W. Horn (Ger. P. 36403), in lieu of the fire-door, fixes a box provided with an inlet-spout for tar and a dish for spreading this out.

P. Mörrh (Ger. P. 38166) sprays the tar by means of superheated steam.

Key (*Engineering*, 1886, p. 750) burns the tar after filtration without compressed air or steam.

Westphal's naphtha burner<sup>1</sup> is specially adapted to a blacksmith's forge-fire. The liquid fuel issues from a group of annular slits, and is sprayed by compressed air. The flame is directed upon the object to be heated by means of a beak-shaped jet. (This apparatus will probably do well for petroleum

<sup>1</sup> *Dingl. polyt. J.*, cclxiii, p. 373.

or creosote only, but would be stopped up too easily when burning raw tar.)

Rispler<sup>1</sup> states the heating value of 100 coal-tar as amounting to 220 to 270 good nut-coal, and points out that the supply of air can be much more exactly regulated than with coal.

Descriptions of the burning of *petroleum-residues* at Baku (where they practically are the only accessible fuel) have been given by Boverton Redwood (*J. Soc. Chem. Ind.*, 1885, p. 78), and by C. Engler (*Dingl. polyt. J.*, 1886, cclx., p. 440).

According to Engler, these residues, called "massud" by the Tatar workmen and "astatki" by the Russians, form 55 or 60 per cent. of the crude petroleum. Some of it is used up for making lubricating-oils; but much more is burned, partly at the works, to supply the heat for distilling and for raising steam, partly as fuel for steamships and locomotive engines, even at a great distance, on the Caspian, the Black Sea, the Volga, on the Transcaucasian and Transcaspian railways, and so forth.

The heating-value of massud is nearly twice that of coal; with burners of the best construction, 1 lb. of massud will raise 12 lb., or with care 14 or 15 lb. of steam. The distillation of 100 parts crude oil for kerosene consumes three or four parts of massud.

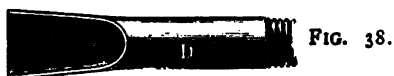
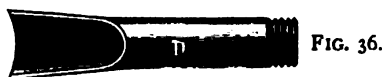
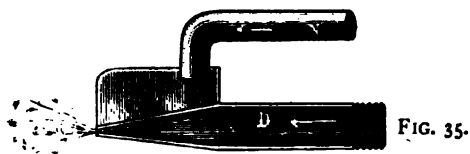
The burners for the residues, called "forsunka," have been principally introduced and improved by O. K. Lenz at Baku. They have very varying forms, but always work so that the oil is atomized by steam previously to burning. The atomizing by compressed air has not answered (*cf.*, however, Nobel's shelf-burner as described below). Along with the steam enough air enters to produce complete combustion, and a temperature beyond the fusing-point of wrought iron. Therefore the boiler-plates, heating-tubes, etc., must be protected against the direct action of the forsunka flame.

A very simple forsunka is shown in Figs. 35 to 38. The 1-in. iron steam-pipe D is flattened at its end to a slot of  $\frac{1}{8}$  or  $\frac{1}{16}$  in. width, through which the steam issues. The residues are conveyed by the pipe N; the thick oil spreads over the cup fixed over the steam-nozzle, runs down over the slit, and is converted by the steam into a fine spray. The

<sup>1</sup> *Chem. Zeit.*, 1904, p. 957.



different nozzles, shown in Figs. 35, 36, and 37, serve to produce a more pointed, or a broader, or a medium flame.



The Brandt forsunka (Fig. 39) somewhat resembles the spray-producer, or "squirting-cock" (Fig. 34, p. 326). The residues, arriving at *N*, and the steam from *D*, are separately carried forward in the tubes *b* and *m*, passing through the brass-casting

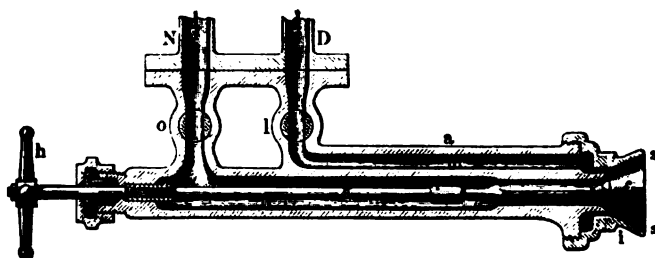


FIG. 39.

*a.* The massud issues through an annular slit, regulated by the cone *f* by means of the handle *h* and spindle *g*; the steam issues by an outer annular slit, concentric with the former. Both are mixed between the cone and the nozzle *i*, and issue at *s s* as a spray, which is lighted. The taps *o* and *l* are left open, the cone *f* serving to regulate the process.

Figs. 40 and 41 show the application of such a burner to an ordinary Cornish boiler. The residue runs from the tank R through the pipe N into the burner; the steam comes from the dome D. At *r* the whole burner can be turned round in a

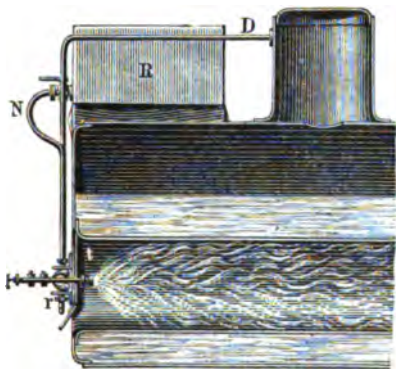


FIG. 40.

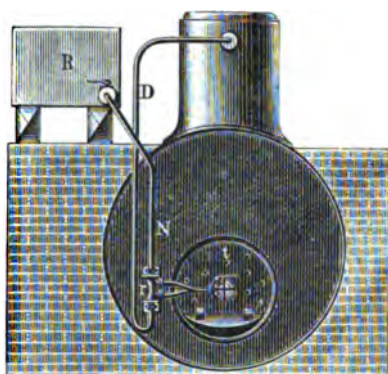


FIG. 41.

horizontal plane, so that on turning it 90 degrees it is clear of the door *t*. In this position it is lighted, in order to prevent explosions, and is then turned back. The necessary air enters through the holes in the door *t*, and through a larger opening provided with a regulating valve.

FIG. 43.



FIG. 44.

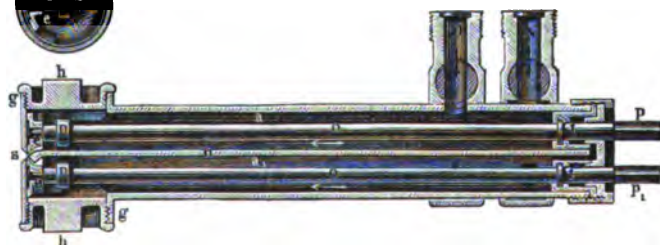


FIG. 42.

The Lenz forsunka is shown in Figs. 42, 43, 44. The double brass-tube *a a*<sub>1</sub> (Fig. 42) ends in the cylindrical mixing-chamber *g*, closed at top and bottom by screw-lids *h h*; the movable rods *o o*, with the key-ends *p* and *p*, turn in bearings at *t* and *u*, and end in eccentric pins (Fig. 43). The latter work in semi-

cylindrical slides *e*, which are moved up or down by turning *p* or *p*<sub>1</sub>, so that they more or less approach the midfeather *b*, and thus exactly regulate the supply of residues and of steam. The oil is converted into a spray, and issues as a sheet of flame through the horizontal slit *s*, which runs rather less than half-way round the chamber *g*. *D* and *N* are taps for shutting off steam and oil. This kind of burner consumes about 3 to 3½ kg. residues, of specific gravity 0.910 and 140° inflaming-point, per horse-power and per hour.

Sandgreen's burner (also used by Nobel Brothers) is shown in Fig. 45. *N* and *D* carry oil and steam into the two halves of

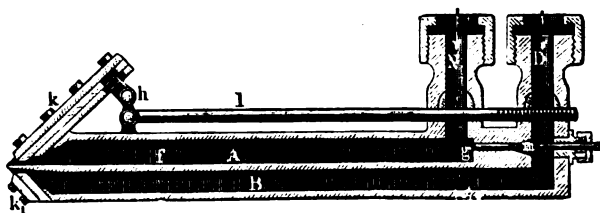


FIG. 45.

the chamber *A B*, separated by the partition *f*. The supply of oil is regulated by adjusting the mouth-plate *k* by means of the lever *h l*, the supply of steam by the mouth-plate *k*<sub>1</sub> set once

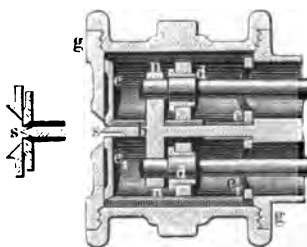


FIG. 46.



FIG. 47.

for all. The cone *m* permits occasionally cleaning out the compartment *A* by steam issuing through *g*.

A different description of burner must be used for locomotive and other tubular boilers, where the flame must be spread out. A Lenz burner for this purpose is shown in Figs. 46, 47,

48, 49. It is very similar to the other Lenz burner, Figs. 42-44, but the slit *s* runs round the whole chamber *g*, except where it is joined to the burner, so that the spray issues in an annular form. Hence the slides *e* and *e*<sub>1</sub> must also be cylindrical, and must move up or down the chamber *g* like pistons. The



FIG. 48.



FIG. 49.

movement takes place by means of the rods *o*, running in bearings *n*, fixed to the partition *b*. When the eccentric rings *d*, attached to *o* (Fig. 48), are turned, the cylindrical slides *e* or *e*<sub>1</sub> are raised or lowered, and thus admit more or less steam or oil through the slit *s*. Fig. 49 is a vertical section through the

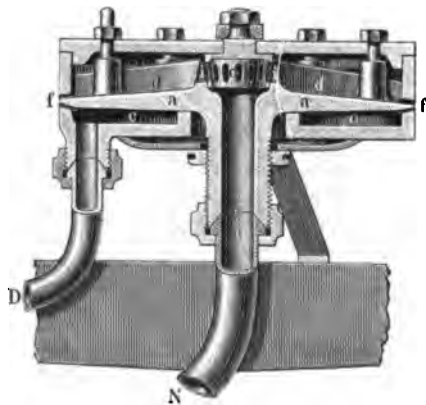


FIG. 50.

supply-pipes, *D* for steam, and *N* for naphtha, etc. The tap *h* allows of sending steam into the oil-chamber for the purpose of cleaning it out. Fig. 46 shows a somewhat different shape of partition and burner mouthpiece.

Figs. 50 and 51 show a Brandt forsunka, as adapted to loco-

motive boilers. The mixing-chamber is divided into two compartments by the horizontal disk *a*. Steam enters into the lower, smaller compartment through D; naphtha, etc., into the

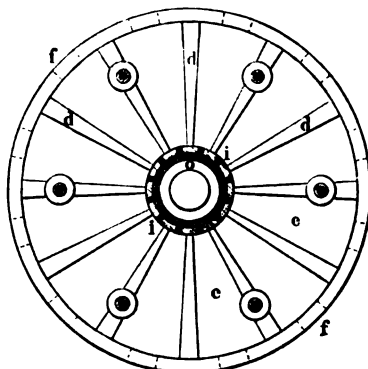


FIG. 51.

upper, larger compartment through N. By slightly turning the cap *o*, the slits *i i* are more or less opened, and the supply of residues (naphtha, tar) can be thus exactly regulated. The

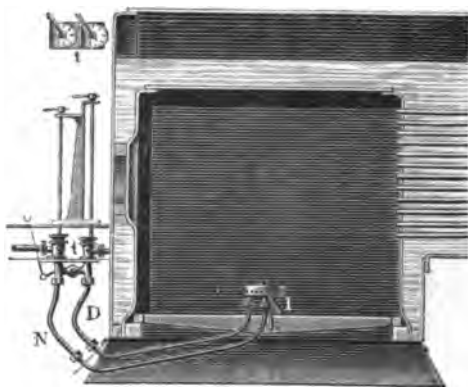


FIG. 52.

latter issue radially between the ledges *d* through the sectors *e* and the slits *f*, and are atomized by the steam issuing below.

Fig. 52 shows the same burner (*l*), fixed in a locomotive fire-box in the centre of the grate (*k*). The consumption of naphtha for the transit of a train of twenty loaded trucks,

according to Brandt, is about 10 kg. per kilometre (say 33 lb. per English mile).

Engler enumerates as advantages of forsunka-firing:—high heating-power, small space for fuel, small volume of the burner, easy working, and, from his own observation, absolute freedom from black smoke in the case of factory chimneys. The locomotive fires are not quite exempt from smoke and smell, but more so than our own, worked with coal. Mr Redwood, in

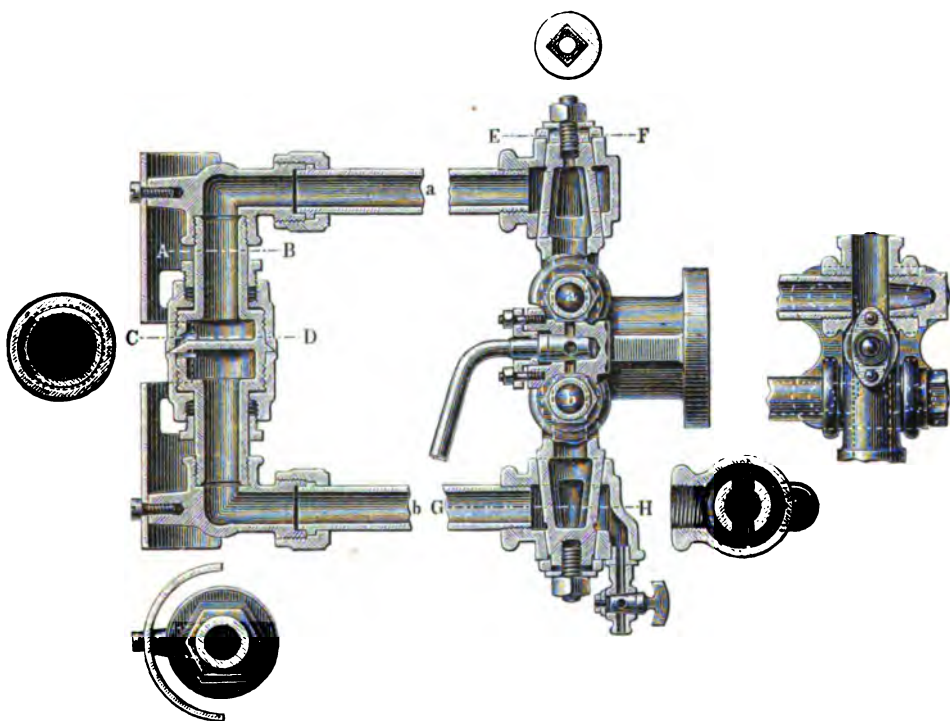


FIG. 53.

travelling on those lines, noticed no smoke, but occasionally a disagreeable smell of imperfectly burned petroleum.

The following astatki burners are mentioned in Redwood's description (*loc. cit.*). In Kaufman's burner (Fig. 53), which has been adopted by the Russian Government for use in torpedo-boats, the oil enters at *a*, the steam at *b*; they meet at *C D*, where, by means of two screws, a fissure is opened through which they escape, a spray being produced. The intensely hot,

pointed flame makes it necessary to employ screens of fireclay in front of the boiler-plate. The roar of the blast is rather objectionable in this apparatus; but, nevertheless, more than a hundred steamers on the Caspian and Volga are fitted with it. There are consequently no firemen or coal-trimmers, but a single attendant, whose duty it is to consult the pressure-gauge from time to time, and to regulate the supply of steam and astatki accordingly. In thus raising steam it is, of course, necessary for a start to take a supply of steam for the blast

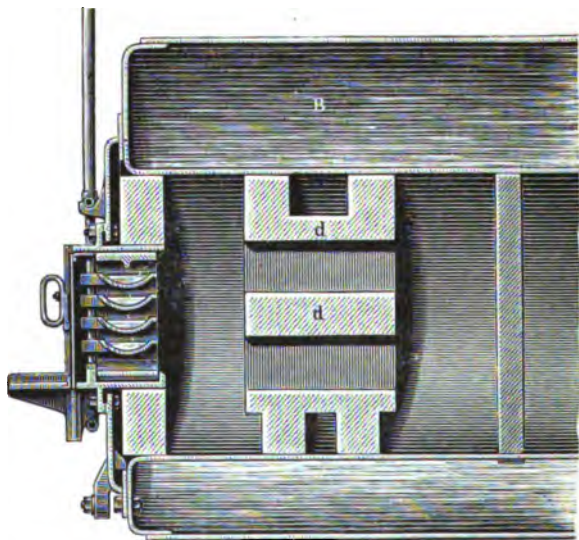


FIG. 54.

from a small auxiliary boiler, or to raise steam by an ordinary fire of wood or coal.

In consequence of the objections attaching to the steam-spraying method of burning astatki, Messrs Nobel have patented an apparatus free from them. This apparatus, as shown in Figs. 54, 55, and 56 (Fig. 54, a vertical section; Fig. 56, a sectional plan; and Fig. 55, a view of the boiler in front: more details of the plant are given by Redwood, *loc. cit.*), essentially consists of a series of troughs so arranged at the mouth of the furnace that the burning astatki flows by successive stages from the highest to the lowest. Air passes in between the troughs and through

the four openings *c*; the direction of the flame is given by the firebrick walls *d d*. With this apparatus 14½ lb. of water can

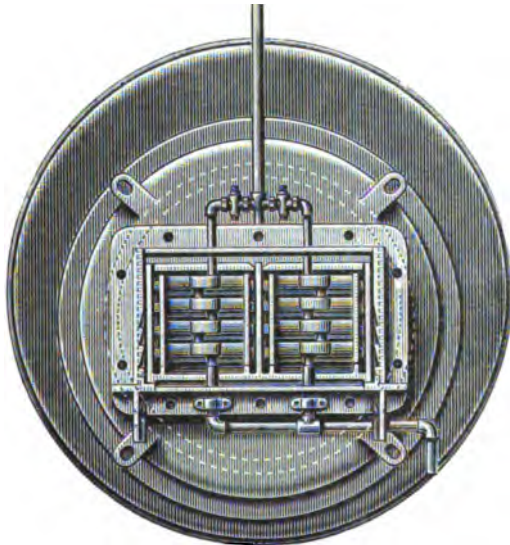


FIG. 55.

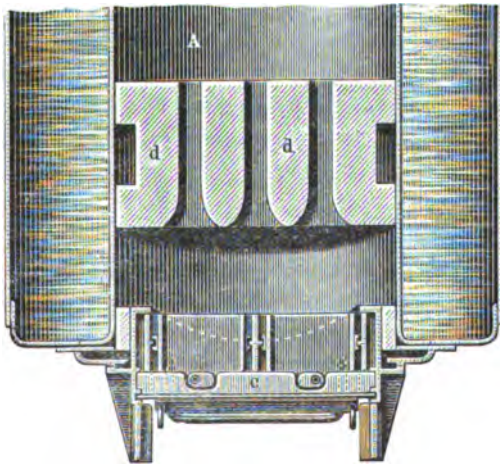


FIG. 56.

be vaporized by the combustion of 1 lb. of astatki, against only 12 lb. by the "spray" method.

Most remarkable results have been obtained with Nobel's  
Y



trough-burner for metallurgical purposes. It reduces wrought iron to a state of fusion; and horseshoes, spanners, toothed wheels, and other articles of soft iron can be thus easily and cheaply produced by casting in moulds, without any heating of the air-supply. With this, no doubt, much higher temperatures might be reached; but the difficulty of finding materials sufficiently fireproof for the furnace stands in the way of making experiments in this direction. The freedom of this fuel from phosphorus and sulphur is a great advantage in metallurgical operations. The price of *astatki* in 1884 was 2s. 6d. per ton at Baku, or about 8s. per ton at Tsaritsin on the Volga; it is largely used in Moscow, and goes as far as Stockholm and Teheran. Greiner (*Trans. Iron and Steel Inst.*, 1915), describes the use of coal-tar for heating Belgian blast-furnaces during the war, when coke could not be procured. The heating of open-hearth furnaces by a tar-spray is described in *Engineering*, 1915, p. 558.

So far as the use of this fuel for steamships is concerned, the economy of space for storage, and the saving of labour and time in placing it on board ship, must be taken into consideration. At the present price of coal-tar it would perhaps pay to use it for other purposes besides heating gas-retorts, in the same way as *astatki*, wherever very great heat or economy of storage is of permanent importance.

Körting's steam-jet spray-producer (*Dingl. polyt. J.*, vol. cclx., p. 411) is much employed. This apparatus, shown in Fig. 57, is made entirely of iron, and therefore very substantial and very cheap (£3). It is claimed that the peculiar kind of steam-supply prevents any trace of tar from falling down. The supply of tar is regulated by a nozzle (A), more or less bored out; it is not easily stopped up, as a strainer (T) and sieve (S) retain the impurities. It is also readily accessible for occasional cleaning by moving up the thimble H. The spray-producer itself can be cleaned any moment by means of the pin R, after removing the cover V. The steam-jet draws air through the box L with very great force; the slides M serve for regulating the air-supply. The steam enters through D, and the speed of combustion is regulated by means of the steam inlet-valve. The tar-cistern is placed on the top of the retort-furnace, so that the tar is always heated and thin.

W. Horn (Ger. P. 36403) patents a simple apparatus for burning tar, etc., which can be hung from the fire-door hinges, and

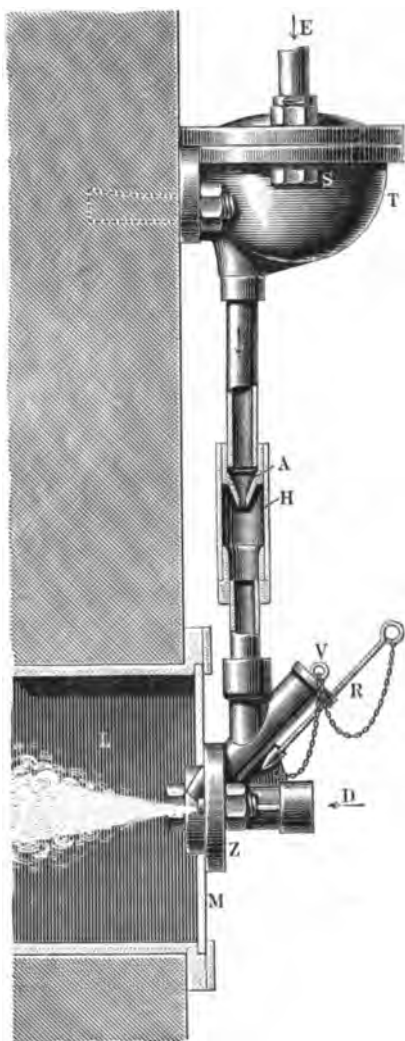


FIG. 57.

is thus easily put in or taken out when a change from liquid to solid fuel is required.

Holden<sup>1</sup> has adapted the process of burning liquid fuel to

<sup>1</sup> *Z. Verein. deutsch. Ingen.*, 1891, p. 496.

oil-tar gas and successfully applied it to the steam-boilers and a number of locomotives on the North-Eastern Railway. He maintains on the grate a 3-in. layer of coal, over which the liquid fuel is sprayed by two steam-injectors (Fig. 58); a second annular steam-jet carries the air necessary for combustion into the firebox. If for some reason the employment of liquid fuel is to be discontinued, coal can be fired without any trouble. The only change to be made in a locomotive to adapt it for liquid fuel is to fit underneath the fire-door two pieces of 6-in. tubing, which pass through the water-space and the copper or iron back-wall of the firebox, and through which the fuel is blown in, as shown in Fig. 58. The steam is taken direct out of

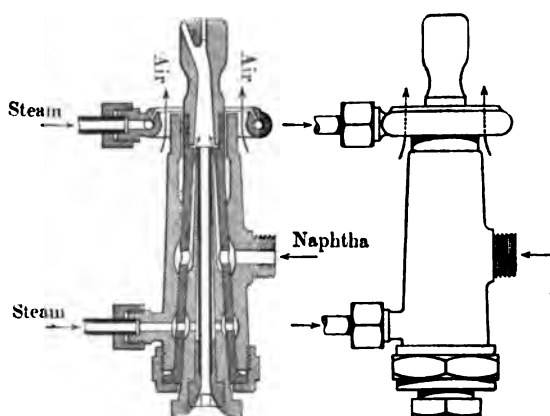


FIG. 58.

the boiler-dome, without overheating. Its supply to the tuyeres is regulated by a tap for both, that to the annular jets by special taps. A special steam-pipe (Fig. 58) admits of heating up the fuel in cold weather. All tar-pipes can be blown out by steam in case of obstructions. The greater part of the grate is covered with pieces of chalk or limestone, so as to admit but little air to the solid fuel from below. This system of heating requires only a slight draught, which has several advantages.

The Great Eastern locomotive shown in Fig. 59 possesses a tank holding a ton of tar, which suffices for a train of 15 carriages running 200 miles in suburban traffic. At the same time 25 cwt. of coal and  $\frac{3}{4}$  cwt. of limestone are used, whilst with ordinary coal about 50 cwt. would be required.

The saving in money is not considerable, but the advantages are that the combustion is smokeless, and the production of steam can be at any time interrupted or started by means of shutting or opening the valves.

In 1902, Bruckmann reports (*Z. Verein. deutsch. Ingen.*, 1902, p. 317) that the Great Eastern Railway of North America used Holden's plan in 88 locomotives, and consumed for this about 85,000 tons of tar—that is, about a quarter of the coal-tar then produced in the United States.

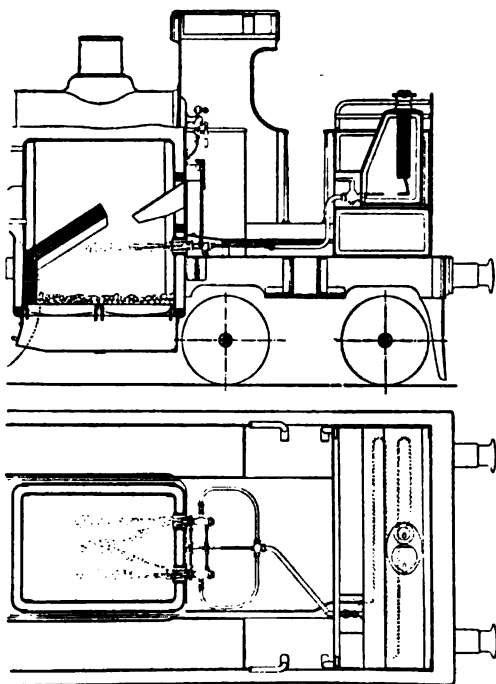


FIG. 59.

We quote also the processes of Busley (B. P. 5026, 1887), Mörtz (Ger. P. 40142), Wrede (Ger. P. 56339), Heyden (*Chem. Trade J.*, 1887, p. 159), Hunt and Mirck (U.S. P. 768368), E. W. Jackson (U.S. P. 777789), Merkens (Ger. P. appl.), Boeddeker (*Z. f. Baubetrieb*, 1910, pp. 1 *et seq.*), Koehn (Ger. P. 209659), Hausenfelder (*Stahl u. Eisen*, 1912, p. 772), Stewart and Perry (U.S. P. 1134421), Markl (B. P. 10383, 1914).

In order to remedy the irregularity of flow produced by the impurities of raw tar, Livesey<sup>1</sup> inserts a number of pieces of  $\frac{1}{8}$ -inch brass tubing in the pipe between the tar-reservoir and the burner. This causes, by friction, a retardation and thereby a regulation of the flow.

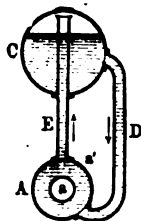


FIG. 60.

For a similar purpose J. Smith employs three lengths of tubing, 3 feet,  $4\frac{1}{2}$  feet, and 6 feet, coiled up into spirals, in order to provide for the changes in the fluidity of the tar and the temperature in the furnace; the level of the tar is to be kept 5 feet above the coils.

Seigle<sup>2</sup> objects to the employment of a single fireplace lined with firebricks. The flame produced by the liquid fuel is driven into water-jacketed tubes, acting like Bunsen burners, the combustion being commenced and finished in the

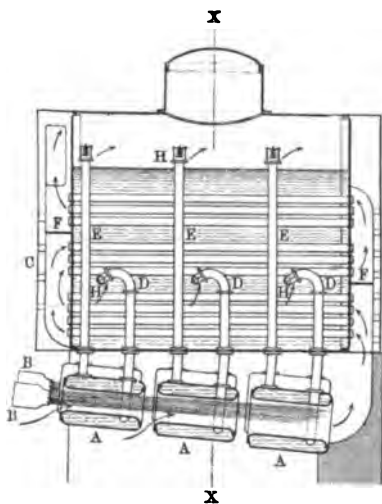
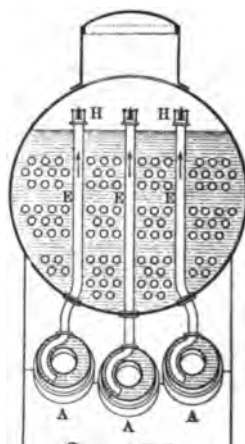


FIG. 61.



Section X-X

FIG. 62.

interior, and colourless hot gases issuing from them, to be utilized elsewhere. As shown in Fig. 60, each tube (A) is formed of two concentric cylinders (*a a'*) with a common bottom. Above these is the steam-collector C, into which the feed-water is introduced by D to the lower part of A; tube E is the outlet for steam

<sup>1</sup> *J. Gas Lighting*, 1886, p. 159.

<sup>2</sup> *Z. f. Berg-, Hütten- und Masch.-Ind.*, 1895, p. 197.

into the upper part of C. Figs. 61 and 62 show the application of this system to a ship's boiler. The apparatus consists of three rows of burners (A) connected with the main boiler by the feed-pipes D and the steam-pipes E. Opposite the first tube of each row there is a spray-producer (B), which drives a jet of lighted gas into three tubes (A), progressively enlarged so that the air for combustion is carried along through the annular free

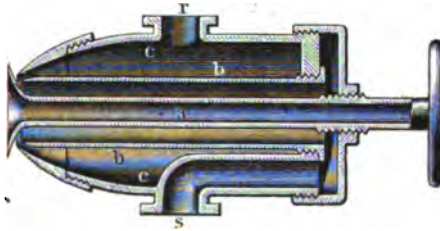


FIG. 63.

spaces between the tubes. The combustion must be regulated so that it is entirely or nearly complete when the gases issue at the end. They then rise upward and pass through the boiler-tubes, their course through the chambers C being shown by the partitions F. The last heat is applied to heating the feed-water, and the gases issue into the air, without a chimney. The



FIG. 64.

combustion of great volumes of gases and vapours in long and narrow tubes offers a good contact with cold surfaces.

Kämpf (Ger. P. 97505) avoids the necessity of using compressed air or steam by employing gases obtained in gasifying combustible substances and burning as well. The liquid fuel (Fig. 63) enters at *r* in a funnel-shaped orifice of the central tube *a* of the set *a*, *b*, *c*, and is sprayed by the gaseous fuel entering at *s* and carried all round *a*.

Ferrari (Ger. P. 56240) avoids the use of spray-producers by

a "box-grate" (Fig. 64), in which the grate is represented by channels, *a, a*. The fuel, contained below a perforated bottom (*b*) or supplied by perforated pipes, is drawn up to the surface of the burner by means of asbestos packing, acting like a wick.

*The Relative Calorific Effects of Coal-tar (with and without Steam) and Coke, for Retort-firing.*

At the meeting of the Gas Institute, London (*J. Gas Lighting*, 29th June 1886, pp. 1242-44), a paper of peculiar interest was read on this subject by F. G. Dexter. To obtain the relative calorific values of tar and coke, Mr Dexter classified the constituents of tar according to their respective boiling-points under the different periods of distillation, and took the average formulæ of the hydrocarbons under these heads as representing the constitution of the oils obtained. The results appear in the subjoined table (p. 345).

Coke, when drawn from the retort and slaked, contains fully 25 per cent. of water, besides the ash and sulphur. Ignoring the impurities, and deducting 25 per cent. for water from the value of fired coke,  $0.75 \times 7000 + 5250$  units per pound of coke are obtained, or, in other words, a relative heating-value for coke and tar of 5 : 8.

By calculating the useful temperatures obtainable from both materials, Dexter arrives at a ratio between tar and coke = 2 : 1 ; but the elements of this calculation are not quite certain, and we would rather act upon the conclusion taken from practice that the above really represents the respective heating-values of tar and coke.

The practical heating-value of tar is due chiefly to its form and the ease with which it is manipulated. It can be introduced in a small constant quantity, and in a condition much more favourable for intimate mixture with the supply of air than is possible with coke, and consequently the excess of air supplied may be much less. The intermittent cooling produced by fresh charges of coke is also avoided, and thus a much higher heating effect is necessarily produced. The use of steam with tar should be avoided if possible, as it tends to reduce the temperature in the furnace.

# COMPARISON OF COAL-TAR AND COKE AS FUEL 345

Constituents.	Average Formula.	Weight per cent.	Boiling-point.	Proportionate Weight of Constituents.		Calorific Value.	
				Carbon.	Hydrogen.	Carbon Units.	Hydrogen Units.
First runnings . . . . .	$C_9H_{10}$	3.0	up to 110°	0.025714	0.004286	200	148
Light oil . . . . .	$C_{12}H_{14}$	7.0	110° to 210°	0.061091	0.008910	474	307
Middle oils . . . . .	$C_{12}H_{20}$	27.0	210° to 240°	0.237073	0.032927	1842	1145
Heavy oils . . . . .	$C_{14}H_{18}$	7.0	{ 240° to 270° and upwards }	0.063913	0.006087	497	210
Pitch (56 per cent.) composed of :—							
Oils. . . . .	$C_{18}H_{10}$	17.5	360° and upwards	0.166336	0.008663	1292	298
Carbon . . . . .	C	27.5	...	0.275000	...	2137	...
Gases and water . . . . .	...	11.0	...	...	...	...	...
				0.829127	0.060873	6442	2108
				0.89		8550	



## 346 USES OF COAL-TAR WITHOUT DISTILLATION

This subject is further illustrated by a paper on "The Utilization of Residual Products in Gas-Works" (see *J. Gas Lighting*, 1886, p. 1247) by Mr J. T. Lewis. The author, in referring to the value of tar, states that in 1883 the price varied from 1s. 8d. to 3s. 4d. per ton of coal carbonized, whereas at the present time tar is worth only 4d. to 7d. The following is the value of tar to tar-distillers, taking the prices of the different products at the current market-value. The various items are derived from two sources, one distiller carrying his process further than the other.

### *Products from one Still of 8 tons of Tar.*

Naphtha, 60 gallons, at 9d. per gallon	. . .	£2 5 0
Light oil, 60 „ at 3d. „	. . .	0 15 0
Creosote, 500 „ at $\frac{3}{4}$ d. „	. . .	1 11 3
Crude anthracene, 1 cwt. . . . .	. . .	1 11 8
Pitch, 5 tons, at 15s. per ton	. . .	3 15 0
Wages on the above	. . .	£2 0 0
Coal . . . . .	. . .	0 6 0
	—————	2 6 0
Wear and tear, rent, etc., not known	. . .	...

Giving about 19s. as the value of 1 ton of tar.

### *Products from 1 ton of Tar.*

Benzene (50/90) . 5 gallons, at 1s. 5d. per gallon	. . .	£0 7 1
Naphtha . . 2 „ at 9d. „	. . .	0 1 6
Carbolic acid . 5 „ at 1s. 8d. „	. . .	0 8 4
Creosote oil . 50 „ at $\frac{3}{4}$ d. „	. . .	0 3 1 $\frac{1}{2}$
Crude anthracene, 30 lb., at 3s per cent.	. . .	0 8 0
Naphthalene . 2 cwt., at 3s. . . . .	. . .	0 6 0
Pitch . . . 11 cwt., at 9d. . . . .	. . .	0 8 3
Sulphuric acid, caustic soda, slack, and labour for working	. . .	0 10 6
Wear and tear, rent, etc., not known	. . .	...

It is thus seen that tar was not at that time very valuable to tar-distillers. In cases where the annual quantity of coal carbonized is below 30,000 tons, the distillation is said to be unremunerative. In considering the utilization of tar for fuel, the author gives the following particulars,

illustrating the varying values of coke and tar in different localities :—

(1) Cost of coke for one furnace, per 12 hours . . .	£0 7 4
Cost of coke and tar for ditto . . .	0 5 2
Saving . . .	<u>£0 2 2</u>

Thus showing a saving of 4s. 4d. for each furnace per 24 hours.

(2) Coke saved in 24 hours, 1 ton . . .	£0 16 8
Tar used, 90 gallons, at 1½d. per gallon . . .	0 3 9

Thus showing a saving of 12s. 11d. per 24 hours. Value of tar as fuel up to 2d. per gallon.

(3) Coke saved, 13 cwt. at 4d., in 24 hours . . .	£0 4 4
Tar used, 68 gallons, at 10s. per ton . . .	0 3 5

Thus showing a saving of 11d. for each furnace per 24 hours. Tar value, 12s. 9d. per ton.

When coke is selling at 5s. per ton, and tar at 7s., the one can be sold as profitably as the other; but in the majority of cases it will pay better to sell coke than tar.

Much less favourable as regards the value of tar are the statements of L. T. Wright (*J. Soc. Chem. Ind.*, 1886, p. 561) according to whom the proportion of steam raised in a Galloway boiler by coke (from Silkstone coal) and by coal-tar was only as 1 : 1·13; in firing the gas-retorts the proportion was 1 : 1·17 when atomizing the tar by steam, or 1 : 1·24 by gravitation feeding.

Wright subsequently<sup>1</sup> reports on comparative trials made for raising steam with coals, coke, tar, or creosote oil, continued for a period of forty-six days, with the following results :—

Class of fuel.	Number of days' trial.	Pounds of water evap. from 12° C. at 40 lb. steam-pressure.	Pounds of water from 100° C. at atmos. pressure.
Notting Top Hard Cannel . . .	11	7·46	8·78
Silkstone Gas Coal . . .	7	8·42	10·01
Coke from Top Hard Cannel . . .	6	8·34	9·91
Silkstone Gas Coke . . .	6	9·49	11·15
Tar steam injected . . .	7	10·70	12·91
Creosote steam injected . . .	9	11·24	13·35

<sup>1</sup> *J. Soc. Chem. Ind.*, 1887, p. 36.

Later on he abandoned the injection by steam in favour of a simple apparatus, consisting of three fireclay slabs, placed in a slanting position in front of an ordinary coke-grate, with channels in between, through which the tar enters, together with air. The fixed carbon of the tar is burned farther on upon the grate. The draught need only be 2 mm. vacuum against 6 mm. for coke. If black smoke is avoided the smoke-gases contain on an average 12.9 per cent.  $\text{CO}_2$ .

Körting<sup>1</sup> also shows that it is not possible to replace two parts of coke by one of tar as fuel. With a good (Muntz) gas-producer 100 kg. of Saar coal is distilled by means of 9.6 kg. coke, 100 kg. of Westphalian coal by 12 kg. coke. These 9.6 or 12 kg., according to the caloric power of the substances in question, ought to be replaceable by 8 or 10 kg. of tar, but Körting was never able to attain this. The principal difficulties are:—that the supply of air cannot be kept near the theoretical without danger of black smoke, and that previously-heated air cannot be employed, because this involves keeping the fire-door shut and prevents observing and regulating the flame. He considers the best plan that of spraying the tar by means of a Körting's injector.

Körting states that in 1886 forty-four German gas-works, producing nearly half of the coal-tar obtained in Germany, were burning tar, and were thus consuming 11,434 tons of tar, equal to 12 per cent. of the total German production. He states that nearly all English gas-works were burning tar equal to 20 per cent. of their total production; but this is contradicted by other authorities, quoting the tar burned only = 1 to 5 per cent. of the total (e.g., Davis in *Chem. Trade J.*, 1887, p. 103).

Kraemer also considers that much more tar is burned in Germany than in England, and that the fuel value of 1.2 against 1 for coal is about right. He proposes burning only the tar from the hydraulic main and from the later stages of gas-making, and keeping the better quality for distillation.

James Hargreaves proposed burning coal-tar as a source of *motive power* in a specially constructed hot-air engine. According to the *Chem. Trade J.* of 11th June 1887, an engine with a working barrel of 25 in. diameter and 18 in. stroke gave 29.7 indicated h.p. with a consumption of 2 gall. of

<sup>1</sup> *J. Gasbeleucht.*, 1886, p. 543.

tar, that is an efficiency of 0.174, equal to the best gas- or steam-engines. Since then very little has been heard of this engine, but if it were successful the problem of disposing of the superfluous tar would be definitely solved.

The use of tar (or heavy tar-oils) in internal combustion engines (Diesel motors, etc.) is specially treated by Drexler (*Oelmotor*, 1913, pp. 125, 309, 433, 563).

Kayser (*J. Gasbeleucht.*, 1914, pp. 200 and 220) discusses at length the use of tar and tar-oil as fuel in furnaces and engines. In furnaces this fuel should be supplied under pressure and then broken up by air streams. A flat stream issuing under pressure appears better than spraying through fine orifices which are easily choked. In the Irinyi apparatus the oil is vaporized in a retort in the furnace, flowing into the retort by gravity. The advantages of tar-oil in furnaces are smokeless firing, simplicity of working, and cheapness. Tar-oil is also used in Diesel engines; and Körting Bros. have a plant of 500 h.p. running with tar from vertical retorts. This works as well as a tar-oil installation while the cost of fuel is less, but a special starting means is necessary. Tar has also been used in furnaces, for coating wood, etc., especially in roof work.

Coal-tar is also used in conjunction with coke-oven gas, for *heating coke-ovens*. According to *Eng. and Min. J.*, 1904, p. 708, this has the special advantage that the heating-gases contain less sulphur. This latter circumstance is also of importance when using a mixed gaseous fuel in Siemens-Martin steel-furnaces.<sup>1</sup>

#### *Application of Tar for preserving Timber, Stone, Iron, etc.*

Coal-tar has always been extensively employed for the *preservation of building-materials* of all kinds. Stones as well as iron and wood can be preserved much longer, and protected against atmospheric influences, by a coating of coal-tar.

For *stones, brickwork, etc.*, especially when exposed to the action of acid vapours, Kuhlmann<sup>2</sup> strongly recommends painting with coal-tar. Long before that, however, it was usual in chemical works to boil the stones intended for erecting acid-tanks, hydrochloric-acid condensers, chlorine-stills, etc., in gas-

<sup>1</sup> *Eng. and Min. J.*, 1904, p. 708.

<sup>2</sup> *Comptes rend.*, lvi., pp. 1006, 1146.

tar somewhat boiled down, also to paint the brickwork of the furnaces and any wood or iron work exposed to acid vapours with coal-tar, nay even to soak the roofing-tiles in the same; and this is done up to this day. It has been noticed at the works that coal-tar not merely renders those objects less liable to be acted upon by damp, acids, etc., but makes the stones much harder and able to resist mechanical wear and tear. Hence the stones intended to be used for acid-cisterns and the like must be completely dressed by a stone-mason before they are put in the tar-pan, as they will not take the chisel after boiling. Fireclay pipes, which in the crude state are not even water-tight and are extremely fragile, after boiling in tar become acid-proof, hard, and very little sensitive to changes of temperature. But there is no reason why the employment of coal-tar in this direction should be confined to chemical works. It has been observed that brick-paving lasts very much longer if the bricks have been first soaked in hot tar. This is also the case with roofing-tiles, and is as good as, though very much cheaper than, glazing them, to make them stand the weather.

On my own recommendation, a large brick-works has extensively employed hot coal-tar for preparing black roofing-tiles, with complete success. But it must be noticed that a mere dipping in ordinary coal-tar is not sufficient to produce a permanent coating of adequate strength. The tar should be heated to at least 100° C., and the bricks or tiles, etc., should be left in it for some time, till, on breaking a sample, it is found to have rather deeply penetrated into the substance of the brick. The tiles are then left to dry for some time, isolated from one another on convenient frames.

For all these purposes the tar should be deprived of water and of its most volatile oils by evaporation or (far more rationally) by heating in a still; and much the best is the varnish or "refined tar" made from pitch and tar-oil (*cf.* Chapter VI.).

Others recommend depriving tar of water, but *not* of the volatile oils, because the tiles otherwise remain greasy for some time; hence the "prepared tar" to be mentioned later on should not be used for blackening the roofing-tiles. These are dipped into the warm tar directly they come out the brick-kiln while quite hot.

The Gesellschaft für Teerverwertung has taken out a Ger. P. (No. 271935) for protecting stones by tarring.

Tar is also employed for *painting metals*. When laid on hot, as frequently practised by blacksmiths, it produces a shining and lasting black coat. Also cast-iron gas-pipes are mostly protected against rusting by a coat of tar laid on hot. That this is regularly practised in chemical works has already been stated. In such cases it does not matter if the coat is rather rough and thick. Should, however, a thin, equal, shining, and lasting coat be required, in the place of raw tar one of the varnishes made from pitch and tar-oils, which are described in Chapter VI., must be employed.

Before painting with tar, iron materials should, if possible, be heated, or else tar entirely freed from ammoniacal liquor must be employed, as the latter induces corrosion of the iron.

The Union of German Iron-founders prescribes that the iron pipes should be carefully cleaned, heated evenly to 150° C., and painted inside and outside with the tar-varnish, which must be heated up at least to 100° C. The coat of paint should be firmly adhering and tough.

When properly made, the protection of iron by purified tar (or, preferably, the tar-varnish described in Chapter VI.) is much better than by the ordinary red-lead and linseed-oil paint, which is not merely gradually destroyed in damp soil, etc., but according to Toch (*J. Soc. Chem. Ind.*, 1905, p. 527), gradually becomes pervious to water.

E. Fischer, in *J. Gasbeleucht.*, 1908, p. 1152, gives special rules for proceeding in tarring cast-iron pipes.

The Aktiengesellschaft für Asphaltierung, etc., formerly Joh. Jeserich (Ger. P. 65239), manufactures a varnish for painting iron by mixing fat-gas tar products with "goudron" or brimstone which, it is asserted, is superior to other similar paints by easily entering into all holes and pores, and by loosening and detaching rust.

Raschig (Ger. P. 30755) forms an emulsion of tar and clay in water which can be employed in the cold state, and which he sends out by the name of "Kiton A." It serves for painting stone, brickwork, cement, concrete, iron, or any other metal, wood, paper, paste-board, or roofing-felt. It dries very quickly, does not remain pasty, and remains hard also when exposed to the heat of the sun. It does away with the danger of fire present in the employment of tar-boilers,

and can be employed by means of painting machines for badly accessible high columns, frames, etc., without the necessity of a stage. "Kiton" contains about 50 per cent. tar, looks like boot-black, and can be diluted with water to any extent without any secretion of the tar in the shape of drops. When the mixture has been standing for a long time, the tar is secreted in the shape of a fine, black powder, which by renewed shaking is again incorporated with the liquid part, forming a new emulsion.

For *preserving wood*, coal-tar was recommended as early as 1799, by Le Bon; but for this purpose it is inferior to wood-tar, which even now is exclusively employed in shipbuilding. Wood-tar penetrates much more deeply into the pores of wood, covers it with a coherent coat, and the preservative action of its phenols is assisted by its paraffin. The drawbacks of coal-tar are its free carbon and its naphthalene. The former prevents the tar from entering the very finest pores; the latter, volatilizing even at ordinary temperatures, leaves gaps in the coat. Some go so far as to say that coal-tar produces interior rotting of the wood; but this has not been positively proved, and the manifold employment of coal-tar in chemical works has never led to such a result. At all events the tar-varnishes are preferable to crude coal-tar for wood-painting also. *Tar vapours* are said to act even better than tar in preserving the wood; this has been patented by Robbins in the United States and by Paradis in Austria (Wagner's *Jahresber.*, 1871, p. 848); the success of this process, however, is more than doubtful, as we shall see when treating of creosote oil. It is unnecessary to say that coal-tar is in any case very inferior to the "creosote oils" employed in the proper way for "pickling" timber, as will be described in Chapter VIII.

Rives (*Dingl. polyt. J.*, clvii., p. 317) proposes as a substitute for wood-tar a mixture of coal-tar, rosin, and lime. A mixture called *sulphur-tar* or *benz-asphalt*, prepared by boiling two parts of sulphur with three parts of coal-tar, has been strongly recommended as protecting wood, iron, and stone against decay and rust. A similar mixture is the *wood-cement*, employed as a roof-covering (Chapter VI.). A mixture of coal-tar with its own weight of hydraulic lime, Portland cement, etc., is said to liquefy at 70°, and to yield on

cooling a soft, pliable varnish, resisting acids and specially adapted for wood under water, water-pipes, and roofing-tiles (Dreyssig, Ger. P. 10685). Wildhagen (Ger. P. of 1885) recommends a mixture of wood-pulp, coal-tar, glue and water, employed in the cold state.

Reilly (Ger. P. appl. R27210, of 1910) applies for the preservation of wood, coal-tar from which the free carbon has been removed by centrifuging.

#### *Application of Coal-tar for the Manufacture of Roofing-felt.*

Roofing-felt seems to have been introduced during the eighteenth century in Sweden by Faxe, and in 1791 in the Tyrol by Kag. Faxe simply covered the roof with millboard and then painted this with wood-tar. Kag prepared the millboard beforehand by impregnating with oil-varnish and dusting it over.

Soon a cheaper material was found in coal-tar, one of the first employments of which was for this particular purpose. In Germany it was first introduced in the beginning of the nineteenth century by Gilly, but without lasting success until about 1840, when several factories were established at Neustadt-Eberswalde and Leipzig, which were soon followed by others, so that the manufacture of roofing-felt in Germany, and later on in America, became a very important branch of industry, consuming large quantities of coal-tar and considerably influencing its price.

A historical survey of the employment of coal-tar for roofing-felt and for roof paints, which are frequently sold by fancy names,<sup>1</sup> is given in the *Asphalt- und Teer-Industrie Zeitung*, 1904, pp. 415 and 431. The consumption of coal-tar for this purpose is very considerable indeed on the Continent and in America.

Several of the German factories work up to 10,000 tons per annum for roofing-felt. This industry is also very important in America, but here coal-tar is frequently replaced by residues from the refining of petroleum.

Special treatises on that industry have been published by H. Köhler, *Chemie u. Technologie der natürlichen und künstlichen*

<sup>1</sup> Of such fancy names we will mention: lindol; firmatin; stegiol; sonnenkönig; solitect; excelsior protection; tectorial; hephæstos; furolin; lava saphire; eternal.



*Asphalte*, 1904; Luhmann, *Fabrikation der Dachpappe und Anstrichmasse*; Peterson-Kinberg, *Wie eine moderne Teerdestillation mit Dachpappenfabrik eingerichtet sein muss*, 1904; Friese, *Die Asphalt- und Teer-Industrie*, 1908. We shall in this place give only a general description of it.

Special investigations have shown that the tar employed in this way is very gradually changed by evaporation, but not at all by oxidation.

The preparation of roofing-felt from single sheets of mill-board was soon replaced by that of rolls of great lengths, dispensing with all transverse joints on the roof, and producing a roofing-material of great durability and extraordinary cheapness.

*Materials.*—The material for this manufacture is formed by rolls of mill-board made of pure wool fibre, about 3 ft. wide. The tar must be pure coal-tar, freed from water. This was formerly effected by heating it in open pans, but is nowadays always done by distilling it in close stills up to the point where no more water comes over, with condensation of the benzol distilling at the same time. This "distilled tar" can be immediately employed for the manufacture of roofing-felt, and is greatly to be preferred to "prepared tar," that is, pitch dissolved in creosote oil. Roofing-felt prepared with the former dries much more quickly than that made with "prepared tar." But the latter is better than the former for painting the roofs when laid, simply because it contains fewer volatile constituents and keeps the roofs more elastic. Lignite-tar, oil-gas tar, or beech-wood tar can be used only when mixed with coal-tar or pitch.

The *sand* required in this manufacture must be as free as possible from clay, and of uniform grain. River sand is better for this purpose than sand got in pits. It must be employed in the perfectly dry state, preferably still warm. In the larger factories the sand is dried by means of mechanically-driven drying apparatus, raised up, sifted, and discharged into the impregnating pans with exceedingly little manual labour.

The following is a description of a complete modern plant for the manufacture of roofing-felt, as built by Wilhelm Lückau, Hamburg. As seen from Figs. 65 and 66, a tar-still is fixed at such a height that the dehydrated tar can be run into the pans

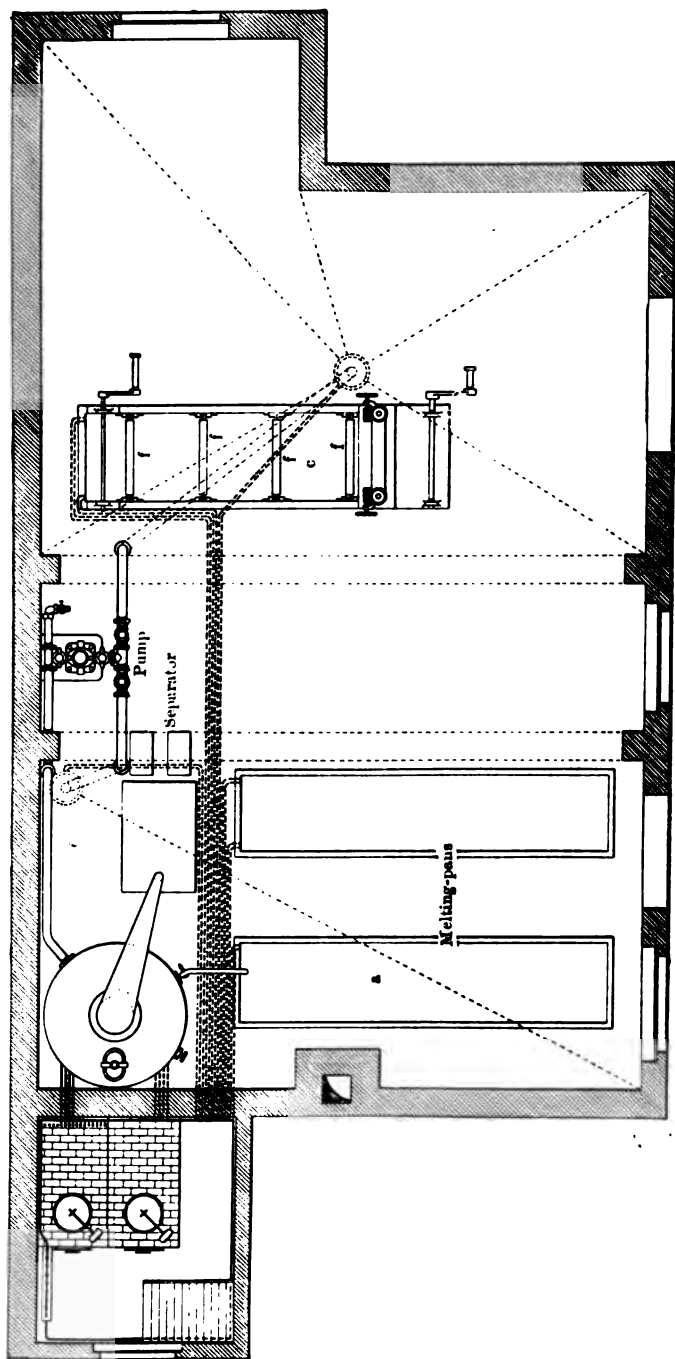


FIG. 65.

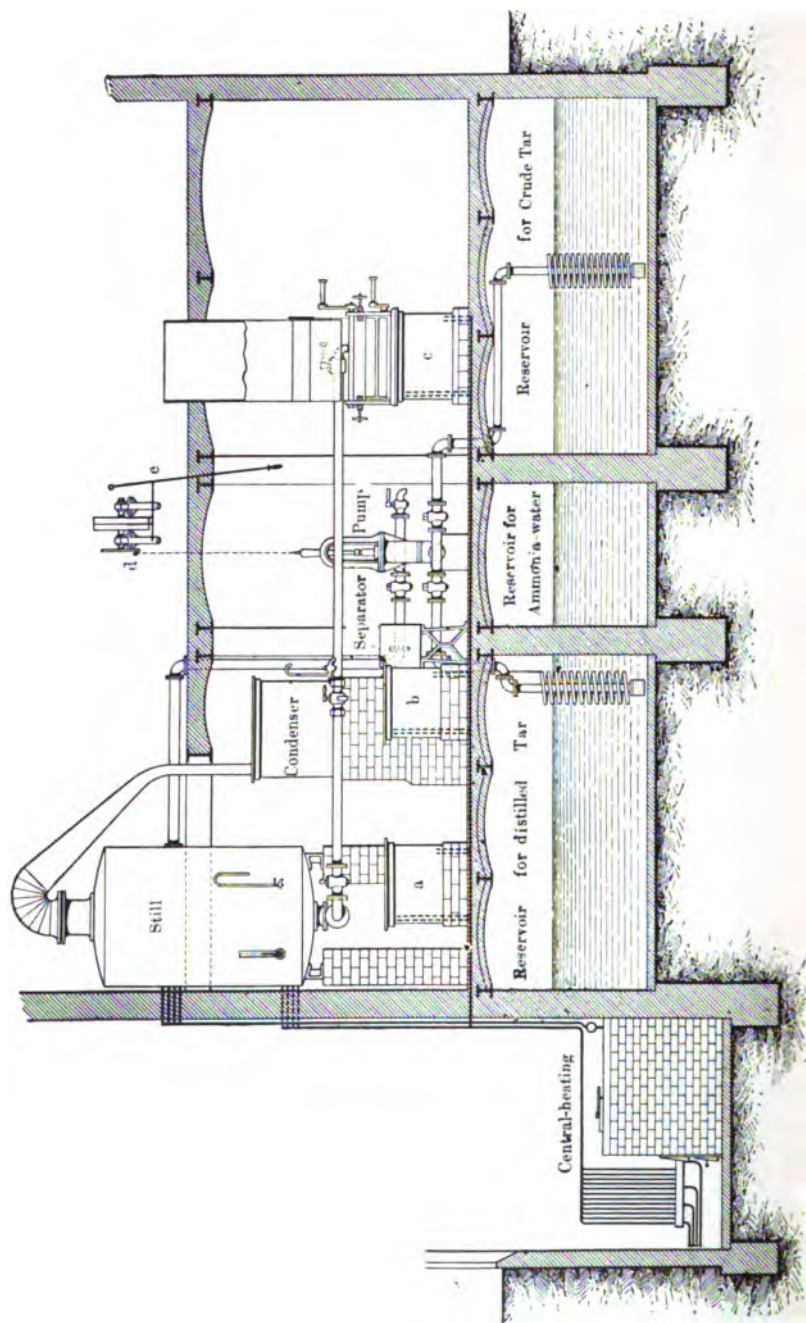


FIG. 66.

*a*, *b*, *c*, or a subterranean reservoir. The still, as well as all other apparatus, is heated by steam. The still is charged from the reservoir by means of a ram-pump, with gearing *d* and *e*, which also serves for another reservoir, containing distilled tar. A tank between these two receives the ammoniacal liquor distilling over. The benzol coming over at the same time runs straight into wrought-iron store-tanks. In order to guard against severe cold, the aspirating-pipes of the pumps are surrounded with heating-coils.

Pans *a* and *b* serve for preparing the cement required in covering a roof with felt, also for wood-cement, etc.; the manu-

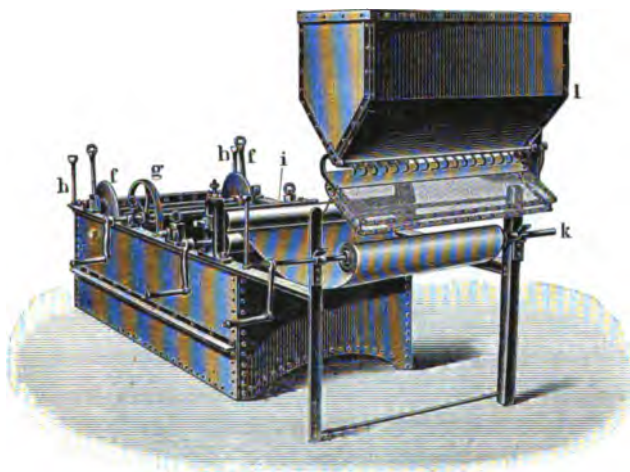


FIG. 67.

facture of the roofing-felt itself takes place in pan *c*. This is a wrought-iron box, 4 ft. wide, 13 ft. long, and 3 ft. 2 in. deep, with a number of removable winding-drums or reels (*f*) for the raw felt. These drums are fitted on one side with a cog-wheel, in which another cog-wheel with hand-crank (*g*, Fig. 67) can be made to gear. Thus one reel after another is charged with felt. The pan is filled with tar to such a height that the felt is at least covered. The temperature of the tar should not be less than 95° or 100° C., because otherwise the felt absorbs too little and the surface becomes greasy.

From the drums the felt passes through squeezing-rollers (*i*),

which can be adjusted by a screw for greater or less distance (Figs. 67, 68). These rollers are made of iron, covered with felt, and are turned by hand. They serve both for taking the roofing-

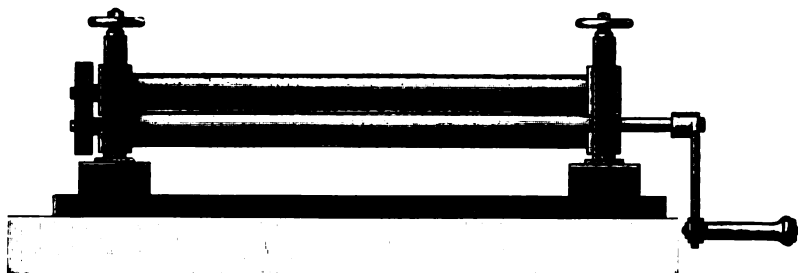


FIG. 68.

felt out of the pan and for removing the superfluous tar. Another wooden roller (*k*) with hand-crank serves for winding up the impregnated felt, after it has been dusted with sand. This roller consists of two portions, fitted together with a



FIG. 69.

slanting joint, so that the felt can be freed by simply pulling asunder the two halves.

The dusting with sand is effected by the apparatus (Fig. 69), consisting of a sand-box (*a*), a spreader (*b*), and sieve (*c*). By *d* the supply of sand can be regulated at will or stopped.

All this machinery is worked by hand. Many attempts have been made to do it mechanically, but without success, as the loosened felt is not sufficiently resistant and the least irregularity causes it to tear, which is easily avoided by a careful man working by hand.

The raw felt is supplied in various strengths from 600 to 2000 superficial feet per cwt. The sand must be sharp—that is, of fine grain and entirely free from clay. It is first dried in the air or by artificial heat, and separated into various sizes by means of a cylinder-sieve. Where good sand is not obtainable, sifted coke-breeze, slag, etc., can be used. In some cases even sawdust is employed. Sometimes felt sanded on one side only or not at all must be made, in which case the squeezing-rollers are placed together as tightly as possible.

A detailed description of the manufacture of asphalt-pipes and roofing-felt, which does not essentially differ from the above, is given by Petersen-Kinberg in a booklet: *Wie eine moderne Teerdestillation und Dachpappenfabrik eingerichtet sein soll*, Wien und Leipzig, 1904, pp. 164 *et seq.*

The firms of Albert Lück, at Leopoldshöhe-Stassfurt, and Heinrich Hirzel, Plagwitz, Leipzig, undertake the supply and installation of complete plant for roofing-felt.

Roofing-felt is employed principally for roofs, either by itself or as a basis for slates or tiles; also for covering wooden partitions, and for pipes exposed to the open air. It is frequently used for insulating brickwork against the humidity of the soil. This "insulating felt" is made from the strongest raw felt; the impregnating mass is made very thick. The squeezing-rollers are placed far apart, and the "sanding" is done with gravel the size of peas. This kind of insulation is preferable to the former method of pouring on a layer of asphalt, for when the brickwork settles down the asphalt splits and admits the moisture from below, whilst the felt adjusts itself to the changed conditions.

Attempts have been made to put the tar at once into the heating-engine where the felt is made, but nothing is known as to the result.

We quote a number of German patents referring to the manufacture of roofing-felt, or to varnishes for impregnating or covering it:—

Otto, No. 3141; Siebel, No. 43349; Jacobius & Sons, No.

54224; Kanert, No. 91809; Andernach, No. 92309; Wangenheim, No. 78047; Roedelius, No. 64680; Gentzen, No. 70852; Richard, No. 73122; Joecks, No. 96094; Hatschek, No. 101453; Hoepfner, No. 103899; Dörr, No. 137507; Nebeling (appl. B41262); Heilpern & Haas, No. 160660.

British patent : Walbinger, No. 11593, 1902.

Sometimes roofs made of tar-felt are subsequently painted with ordinary oil-paint. This is a mistake, unless the felt has been previously covered with an insulating layer of quickly drying varnish or of blood and slaked lime, which must be allowed to harden before the oil-paint is laid on.

### *Coal-tar as a Cementing Substance.*

Raw tar is much less used for this purpose than pitch and other articles manufactured from it. It appears, however, in that function in a good many patents.

Formerly raw tar was frequently used for forming blocks from small coal, called *patent fuel (briquettes)*. It has now been generally replaced for this purpose by pitch, which is much better suited for it, and of which we shall speak in Chapter VI. A new German patent (No. 170979) in this line has been granted to Shedlock. Possibly that is the process mentioned in *Progressive Age*, xxv., 469, as practised in a place in South Wales, where it is claimed they use only 5 per cent. tar instead of 8 or 10 per cent. pitch—a most doubtful assertion! No account of the *quality* of the patent fuel obtained in this way is given.

J. Alexander (Ger. P. 281398) manufactures briquettes from coke powder, with or without admixtures of wood chips, by means of tar obtained in the production of gaseous fuel from fatty substances, at a pressure of 100 atmospheres, preferably with addition of the soot precipitated in the retorts and pipes.

Coal-tar is used for cementing pulverulent substances to form solid blocks by Cl. Dörr & Co. (Ger. P. 137567). These substances, sawdust, sand, pebbles, are added to the tar, heated up to 150° C., and the mixture is further heated to 150° to 200°, until from 7 to 10 per cent. of the tar has distilled off. We come back to this when treating of the employment of tar in road-making. Similar methods are described in Rubitschung's Ger. P. 144457, and in several others which will be more appropriately treated in Chapter VI.

Mathies & Co. obtained a Ger. P. 163002 for improving coal-tar as a cementing substance by the addition of micaceous iron ore and "mineral-oil varnish."

Eiseler (Ger. P. 59244) combines coal-tar with bone-charcoal and fibrous matters under pressure to form a cement for making joints.

The "basic lining" in the Thomas and Gilchrist steel-making process is also made by the help of coal-tar.

According to Ger. P. 48701, it can be used in preparing the sand for moulds in casting iron.

Daischner (Ger. P. appl. D11210) and Culmer (Ger. P. appl. C8303) applied for German patents for the use of tar as a cement in the construction of furnaces for sodium carbonate and sulphate—an application which has been known and practised for many years.

#### *Application of Coal-tar for Making and Improving Roads.*

Of recent years coal-tar has very largely come into use, both for manufacturing various descriptions of "asphalt," from which roads are constructed, or on ordinary roads, for improving these and especially for keeping them free from dust.

Special treatises on the formation of street-dust and its prevention are: Bernhard, *Untersuchungen über die Ursachen der Bildung des Staubes auf Kleinschlagstrassen, etc.*, 1908; Andés, *Die Beseitigung des Staubes*, 1908.

Special periodicals: *Rauch und Staub, Asphalt-und Teer-Industrie Zeitung, Bitumen.*

For this purpose both raw tar is used and such as has been "prepared" by dehydration and in other ways which will be described later on. Coal-tar has been used for road-making for many years past in France and in the United States (according to Pennock, in 1903, 16,000 tons of tar were used for this purpose in the United States), and recently it is coming more and more into use in the United Kingdom, in Germany, and in other countries.

In Great Britain in the year 1907 only 100 miles of road had a covering of tarry mixtures; in 1908 this rose to 700 miles; in 1909 to 3000 miles; in 1910 to 7000 miles.

In that country the tar process has been quite generally introduced, and all road-improving authorities are now fully



convinced of its success. The county of Kent has made the greatest progress in this direction; then follows Surrey, and altogether all highways starting from London are now tarred, and therefore free from dust. In Scotland also progress is being made in this direction. At first some public boards resisted this movement, on account of the expense; but experience has shown that tarred roads go much longer without repairs than others (cf. *J. Gas Lighting*, 1909, p. 808).

The second International Congress of Roads, held at Brussels in August 1910, has also pronounced in one of its final resolutions that the surface-tarring of roads has to be considered as finally introduced into the road preserving practice.

Burschell<sup>1</sup> gives a detailed paper on this subject. Apart from former trials in this direction, this matter was seriously taken in hand in the South of France by Guglielminetti and Schottelius. At Monte Carlo a very good result was attained, at no higher cost than by the old system.<sup>2</sup> Burschell attained similar results. The road looked like half-asphalted; the surface was smoother, the noise was greatly diminished. In Würtemberg, also, Braun attained very good results. There they employ as a first preparation a "thin light tar-oil," spreading it with watering-cans and brushes. The macadamized road should be as dry as possible; the oil then penetrates  $1\frac{1}{2}$  to 3 in. downwards, and about .3 lb. of it is used for each 10 sup. ft. Now the tar is put on, beginning from the central part of the road; it is heated up to 70° to 90° C., spread uniformly, and brushed in. For each 10 sup. ft., 4 to 5 lb. tar of sp. gr. 1.2 is used, when the road had not been oiled; in the other case only about 3 lb. This process is also very useful for the side-walks. In any case the roads must then be covered with sieved road-dust, and it is all the better if the process is repeated. Braun's process costs 3d. per 10 sup. ft., if 3 lb. oil at 1d. and 3 lb. tar at  $\frac{1}{2}$ d. have been used. According to Burschell, this is less than the cost of the ordinary road-metal, consisting of granite smalls. The tar penetrates  $\frac{1}{2}$  to 1 in., and produces a tough, elastic, water-proof service.

Brix<sup>3</sup> reports very favourably on the success obtained by tarring roads. He recommends heatable spreading-cars. The

<sup>1</sup> *J. Gasbeleucht.*, 1905, p. 1033.      <sup>2</sup> *Ibid.*, 1903, p. 868, and 1904, p. 801.

<sup>3</sup> *Ibid.*, 1904, p. 801.

quantity used should be  $\frac{1}{2}$  gall. per 10 sup. ft. The roads should be dry during the tarring, and the weather should keep dry immediately after it.

Mallet and Payet (*J. Gasbeleucht.*, 1904, p. 945) report similarly about this process as used in France. They recommend an addition of 3 to 6 per cent. heavy oils to the raw tar.

*Raw tar* is decidedly inferior to "prepared tar" for this purpose, as proved by comparative trials in the city of Cologne (*Asphalt- und Teer-Industrie Zeit.*, 1905, p. 20).

Andés (*loc. cit.*, p. 147) states it as finally proved that all *ammoniacal water must be removed* from the tar, both in order to make it less disagreeably smelling, and to prevent those places in the road which are impregnated with water from taking up the tar. Anyhow the tar must be sufficiently liquid to penetrate as deeply as possible into the road-covering.

*Special prescriptions for the quality of the tar for spreading on roads* have not been issued by public authorities, except in the United States, where rules for the limits of the specific gravity, the percentage of fixed carbon, the intervals of distilling, the viscosity, and the yield of pitch have been issued. J. Weber Smith (*J. Gas Lighting*, 1911, xciv., p. 169) gives the following specification for the English road-tars. The tar is taken from gas-works or coke-works. The gas-tar is to be obtained from pure coal, and not to contain more than 15 per cent. of water-gas tar. It should have the following properties:—

	Ordinary tar.	Thick tar.	Soft pitch.
Specific gravity at 15°, estimated in small flasks—			
Average . . . . .	1.195	1.220	1.278
Not below . . . . .	1.185	1.210	1.265
Not above . . . . .	1.205	1.230	1.290
Results of distilling in a retort (thermometer bulb in the distilling-tube)—	Per cent.	Per cent.	Per cent.
Below 210°. . . . .	...	...	...
Below 280°. . . . .	10	7	3
Below 350°. . . . .	35	25	18
Percentage of Naphthalene, <i>in maximo</i> . . . . .	7	6	5
Free Carbon, <i>in maximo</i> . . . . .	15	17	18
Ashes . . . . .	0.5	0.5	0.5
Loss by evaporation at 60° F. in a layer of $\frac{3}{8}$ in., during a week, <i>in maximo</i> . . . . .	2	1.5	1
After another week, when kept at 110° F., the loss should not exceed . . . . .	8	3.5	2

It must be borne in mind that all the rules laid down for the quality of road-tars have been derived from experimenting with special tars, and that they must be accepted with all reserve, for it is well known that the success of road-tarring depends not merely on the quality of the tar used, but even more on the accidental circumstances during the tarring experiments, especially the temperature and state of humidity of the air, and on the state of the road, in respect of dryness and the dust.

To be sure, objections have been raised on various sides against the tarring of roads, more especially against "surface-tarring." It is contended that the trees and other plants in the neighbourhood of tarred roads are gradually killed, that the eyes of the people on such roads are injuriously affected, and that even the durability of tarred roads against heavy traffic, motor-cars, etc., is less than that of ordinary stone or macadamized roads. The reports on these points are very contradictory, but the complaints made seem to apply much less to "inside tarring"—*i.e.*, the employment of proper tar-macadam or artificial stones like that to be described *infra*.

*Doerrite*.—Much attention has been given in Germany to an *artificial stone for road-making*, patented by Klemens Dörr, of Germershausen u. Rh. (Ger. P. 137567 of Dörr, and 144322 of Rubitschung, cf. *supra*, p. 360), and known as *doerrite*. Although this is generally manufactured by means of "prepared tar," *i.e.*, such as has been heated up to 140° to 160°, or of pitch, as we shall see hereafter, we will give its description in this connection. The tar is mixed with assorted gravel, previously dried, in heated drums; the mixture is moulded by means of a pressure of 4 atm. into plates or bricks which are cooled by water on the carrier band. They consist of 17 to 20 per cent. tar and 83 to 80 per cent. silica. At the time of that report they were produced at a rate of 4000 tons per annum. The plates have a rough surface, and therefore are very well adapted not merely for side walks, but also for stables; they are quite water-tight, and form a warm flooring. At Stuttgart the same material is used for jointless roads. For this purpose it is put on in a warm state, rammed in, and rolled after three or four days. In that city they employ basalt smalls and prepared tar, and give the plates a thickness of 4 in.; the cost is 5s. per

10 sup. ft. They claim for it the following advantages : freedom from noise, avoidance of slipping, resistance against water and alkaline liquids, and inconsiderable wear and tear.

Many reports have been made on tar-pavements in various parts of Germany. In France a special Société de Goudronnage des Routes has been established (17 rue de Bourgogne, Paris), which extends this process more and more every year.

The *process of road-tarring* is generally the same, with small variations. The tar is heated up to some extent ; some prescribe  $70^{\circ}$  to  $90^{\circ}$ , others,  $100^{\circ}$  to  $120^{\circ}$ , others  $135^{\circ}$ . The surface of the road is cleaned from dust, the tar is spread on it, and is evenly distributed by suitable means. The operation must be carried out during dry weather, and in warm days, most suitably after warming up the road surface by heated rollers. A damp surface does not take up the tar very well ; on a cold surface it thickens by cooling, and the greasy mass formed causes much trouble by adhering to the wheels of the vehicles.

The spreading of the hot tar on the roads is now generally performed by specially constructed machine-cars worked by horses or electro-motors. The tar is converted into a fine spray and is laid evenly on the road in a width of from 3 to 5 ft., either by means of brushing-rollers or by conical spraying-tuyeres under a pressure of from 7 to 15 atmospheres. In most cases the force-pumps are worked from the axles of the tank-car holding from 1 to 5 tons of tar, which is heated on open fires or by steam-jets. Suitable machinery for this operation is described in many patents and price-lists. Frequently the tar is made thinner by mixing it with creosote oil.

The quantity of tar required for this purpose varies from 1 to 3 lb. per superficial yard.

After the tar has been laid on, the road must be kept clear of traffic for a few hours, in order to allow the tar to penetrate below the surface, to a depth stated from half an inch to 2 in. and more. It is then covered by a thin layer of dry sand, or of the dust previously removed from the centre to the sides of the road (where it is useful in preventing any running-off of the tar during the spreading operation). A properly tarred road looks almost like asphalt. There is much less noise caused by the traffic and practically no dust. Such tarred roads keep much better than the ordinary macadam, and the

greater expense in comparison with the latter is more than counterbalanced by the saving in the cost of maintenance. But a preliminary condition is this: that there should be a certain period of dry weather before and after the tarring—this being an unavoidable drawback of the process.

A much more efficient way of road-tarring, both in respect of the keeping up of the road and of permanently doing away with the dust nuisance, now very much employed in the United Kingdom and the United States, is the bringing on the tar coat below the road-surface. This procedure is carried out, either by putting a thick coat of tar on to the coarse gravel and laying on this the not-tarred fine gravel, without subsequent tarring of the surface; or by tarring the surface material before putting on the coarse gravel. The latter way is known as the "*tar mac*" process; it seems to be the best of its kind, giving to the road the appearance of cast asphalt, very easily cleaned, quite free from dust in dry weather and from mud in rainy weather, the surface remaining in a rough state, and being less slippery than asphalt roads.

The mixture of the various substances required for tar concrete must be so intimate that every particle of gravel or sand is completely covered by tar, without any excess of the latter, which would cause the concrete to be too soft. Some engineers bring on the tar concrete directly after its preparation; others prefer leaving it alone for three or four weeks before laying it on to the roads.

We can mention only a few of the numerous processes of this class described in patent specifications and periodicals, without any prejudice to other processes not described here.

The Northern Quarries Company, Ltd., at Grange-over-Sands, in the year 1904 patented a special process of tar-macadam, named the "Quarrite-Pavement" (Ger. P. 174971), by means of specially painted mixing machinery (Ger. P. 177940). Their machinery is so strongly built that it resists the heaviest traffic and is insensible to heat. The mixing-cylinder is horizontally placed, and about one-third of the top is left open; on the top there are three spouts running all along, the central of which receives the tar, the side spouts receiving coarse and fine gravel. Special means are provided for dropping those materials into the cylinder-pan

all along, quite evenly and in proper proportions, and thoroughly mixing it up in the pan in an extremely short time, after which it is discharged into wagons by turning the cylinder 180°. The United States patent for this process has been taken out by Warren Brothers, the German patent by the Deutsche Quarrit- und Bithulithic-Pflaster G.m.b. H. Powell (*J. Gas Lighting*, 1905, p. 554) makes a favourable report on this process, as carried out in the United Kingdom. The cost of the apparatus is £400. The daily output of 35 tons of quarrite requires 25 cwt. coal-tar, 4 cwt. pitch, 5 cwt. coke, at a total cost of 4s 2½d. per ton of gravel, exclusive of interest and depreciation. Whilst before employing quarrite, the roads had to be repaired every three years, they now stand seven or eight, and even up to ten years, and are entirely free from dust and dirt.

Raschig's "Kiton," a mixture of tar and clay, has been already mentioned on p. 351, in connection with the painting of wood, stone, etc. (Ger. P. 216212). For road-making not less than 2 kg. of Kiton (corresponding to 1 kg. of tar) per superficial metre is to be diluted with three to four times its weight of water. This should be done immediately before putting it on to the gravel, and a covering of sand rolled upon it. It can be also used for finished roads as preventative of dust. Roads treated with a 10 to 20 per cent. solution of Kiton remain free from dust between one and four weeks, corresponding to the traffic.

Nowicki (Austr. P. appl. 7635, of 1909) employs the waste liquor of sulphite-cellulose factories, intimately mixed with half its weight of coal-tar or tar oils (which mixture can be diluted with any quantity of water), for keeping roads free from dust.

Wallbaum (Ger. Ps. appl. W33462 and 35262, of 1909) prepares an emulsion, from tar, pitch, etc., by fusing these substances with rosin, naphthenic acid, etc., and pouring the mass, while hot, into a boiling solution of soap, containing free alkali.

H. Jack (B. P. 24023, of 1913) removes from coal-tar, intended to be used for tarring roads, the naphthalene and phenols (which tend to make it crystalline and corrosive) by heating up to 90° or 100°, then mixing it with anthracene or anthracene oils, and passing a current of air through the

mixture until the desired degree of viscosity has been attained. The addition of anthracene may go up to 90 per cent. of this.

Rhodes and Glossop (B. P. 5813, 1914) describe a filter for the tar used in spraying-apparatus for tarring roads.

*Asphalt and Pitch from Coal-tar without distilling it.*

As far as such substances are made from products obtained in the distillation of tar as residue in the stills, we shall treat of them in Chapter VI. Here we only treat of such processes as are employed for converting raw tar into solid or semi-solid substances of a prevailing organic character, similar to asphalt and pitch.

Trainer (Ger. Ps. 134109 and 138001) heats wood, coal, etc., with tar under pressure, and thus obtains a kind of pitch.

Coulson (B. P. 2102, of 1904) prepared a solidified tar by heating tar with sulphuric acid.

Stringfellow (B. P. 736, of 1894), mixes 100 tar with 100 water 1 alkali and 10 petroleum, thus obtaining a light red oil, then soft pitch, which can be used in shipbuilding, and an aqueous liquid. When mixing the whole before separation with dry lime and clay, an asphalt is obtained, which can be used for paving.

Leaver (B. P. 17209, of 1909) drives off the oils from coal-tar up to the temperature of 360° F., runs the mass remaining in the tar-still into a heatable stirring-apparatus, and treats it in this apparatus at a temperature of 200° F. with sulphuric acid up to the consistency required.

Wendriner (Ger. P. 170932 ; B. P. 4427, of 1906) also heats tar or tar-oils with sulphuric acid, but he adds to this a treatment with hot steam up to the point where the sulphonc compounds are hydrolyzed, and a residue is obtained, practically free from sulphur, neutral and insoluble in water. This is mixed by fusion with the hydrocarbons driven off by the steaming, in order to obtain a product of the desired degree of viscosity.

Sulphuric acid is also employed by G. von Wirkner (B. P. 13185, of 1903 ; Ger. P. 158731). He heats tar or tar-oils with from 10 to 100 per cent. sulphuric acid of sp. gr. 1.71 to 180° C. or above, until the sulphuric acid is decomposed, and the volatile

substances have distilled off to a sufficient extent so that the remaining pitch has the intended degree of hardness. If more sulphuric acid be used, substances are formed which have no more the character of pitch, or the carbonization goes too far.

Frances Merrill (Ger. P. 160617) heats the 85 coal-tar with 10 per cent. water and 5 per cent. ferrous sulphate to 300°. Thus pitch is obtained which is brittle, easily reduced to powder, and easy to mix with the small coal for briquettes, without the trouble caused by the employment of sulphuric acid through the escape of acrid gases.

The Société anon. des Combustibles industriels at Haine St Paul (B. P. 16182, 1905; Ger. P. 161950) makes pitch from tar by treating it with ozone or chlorine peroxide in the presence of alkalis, lime, or dolomite. Ozone is also used for this purpose by Breydel (Ger. P. appl. B58801, of 1912).

The Chemische Fabrik Flörsheim, Dr Nördlinger (Ger. P. 171380), employs the oxidising action of air. He had previously applied this to getting pitch-like substances from wood-tar (Ger. P. 163446), and he now extends this to coal-tar and tar-oils. His process consists in heating the tar to about 120° to 150° C. in the presence of air, oxygen, or ozonised air, until the product shows the desired properties.

Trillich (Ger. P. 200524) stirs 12 parts of dried and sifted spent gas-lime into 100 parts of dehydrated tar, and thus obtains an asphalt-like pitch easily soluble in benzol.

Rudolf Rütgers had already, in 1904 (B. P. 23680, 1904), described a process for the manufacture of pitch from heavy tar-oils by introducing heated air into the hot tar-oils. Later on (B. P. 3192, 1906) he shows that this process may be applied to the tar itself by heating it directly while air, or other gases containing oxygen, or ozonised air are introduced into it. The first heating of the coal-tar drives out the light oils, carbolic acid, and pyridines; later on the intermediate oils are driven out with naphthalene, and at last the residue is converted into pitch. The process may be accelerated by the presence of catalytic bodies, such as copper salts. When applying the air for six hours at 220° C., a more viscous and less odorous product is obtained. By continuing the heating, intermediate products, and at length brittle hard pitch may be obtained. The process differs from known processes by producing a maximum of pitch,



through limiting the distillation and regulating the temperature in such manner that as much as possible remains in the retort, where it is converted into pitch by the action of hot air. In the ordinary distillation of coal-tar only that pitch is obtained which forms part of the raw tar; but by this process the distillable portion of the tar is also to a great extent converted into pitch.

Peck (Ger. P. 124629) makes artificial asphalt by heating a mixture of 50 parts tar, 50 rosin, and 50 petroleum residues at 160°, and further at 177°, whereupon from 3 to 6 parts of brimstone are added to it.

Gasset (Fr. P. 327959) prepares a surrogate for indiarubber by heating 120 parts coal-tar with 25 parts boric acid, and passing oxygen through the mixture.

Mariott (*J. Gas Lighting*, 1907, p. 694) evaporates coal-tar to the requisite consistency and mixes it with dry, pulverulent china clay, thereby obtaining a solid, tough substance which he calls "vulco-bitumen," and which, he states, is of the same quality as the best bitumens from Lake Trinidad.

G. Blass & Son (Ger. P. 174249) solidify coal-tar by the addition of anthracene residues, anthracene, or other high-boiling hydrocarbons.

The Patent Block-tar, Motor-oil and Asphalt Co. prepare coal-tar in block-shape by a special process (*Engineering*, 1909, p. 85).

The Tar Patent Solidifying and Distilling Co., according to *Chem. Trade J.*, 1907, xl., 191, distil off the water and crude naphtha, and run the residue, while hot, into a vessel, where it is mixed with 5 per cent of a material (such as granite chip-pings), which causes it to solidify, and thereby renders it more portable. The solidified blocks may be used for all the ordinary purposes of gas-tar, or of pitch in the manufacture of briquettes, and the light oils are still obtained from the material as in the ordinary process of tar-distillation.

Abderhalden (*J. Gasbeleucht.*, 1915, p. 140) tried to isolate the high-boiling oils of coal-tar without fractional distillation. If coal-tar is mixed in the cold with the same weight of benzene (petroleum spirit), two layers are formed, viz., a viscid, almost solid pitch and a supernatant liquid containing the benzene and the ordinary tar-oils. The author calls the lower stratum

"pitch-oils." They can be obtained both from tar and pitch, and form a light, inodorous, chocolate-coloured powder, fusing at  $193^{\circ}$ , containing 94.32 per cent. carbon, and 4.06 per cent. hydrogen, corresponding to the empirical formula  $C_{79}H_{40}$ . It boils in a vacuum of 55 mm. mercury at about  $350^{\circ}$ , without sensible decomposition; at atmospheric pressure the boiling-point is about  $400^{\circ}$ , and there is much decomposition and evolution of gas. This "pitch-oil" forms an emulsion with free carbon which is destroyed by dissolving it in benzene, which causes the carbon to separate.

Davis and Windsor-Richards (U.S. P. 1148011) separate constituents of coal-tar by acidifying it with sulphuric acid and extracting with kerosene.

*Coal-tar and Preparations from it for Antiseptic and Medicinal Purposes.*

The antiseptic property of coal-tar has for a long time been known and utilized; its action as a paint on wood depends partly upon this. No doubt it results from the fact that tar kills the lower organisms. For this reason it has also been tried against the potato- and grape-disease; but in these cases the cure may be worse than the evil. Vines treated with coal-tar or the heavy tar-oils mostly yield objectionably flavoured grapes, and the wine made therefrom is affected in a similar manner.<sup>1</sup>

E. Koch has patented a mixture of tar with gypsum, sand, lime, silica, or aluminium silicates, as an insecticide manure, and for preserving corn, other seeds, and the roots of vines from the ravages of insects (Ger. Ps. 14616 and 18637).

Coal-tar is also used for painting the wooden floors of hospitals, barracks, workmen's dwellings, etc., in order to render them water-tight, and to diminish the danger from germ-infection. One kg. of coal-tar suffices for a surface of 10 sq. m. = 107 sq. ft.<sup>2</sup>

Tar, or mixtures containing it, is frequently used for disinfecting cesspools, sewers, etc. Best known in England is

<sup>1</sup> Cornu (*Comptes rend.*, 2nd October 1882). Watson Smith (priv. comm.) has met with a similar objection in the case of celery grown by the aid of manure made from vitriol-tar and lime.

<sup>2</sup> *Gesundheits-Ingenieur*, 1886, p. 434.

MacDougal's disinfecting-powder (consisting of 100 slaked lime, 10 coal-tar, 15 magnesium chloride); in Germany, Süvern's disinfecting-mixture (100 slaked lime, 15 coal-tar, 15 magnesium chloride). No doubt raw tar is inferior in this respect to the specifically disinfecting-substances it contains, such as phenol and naphthalene.

According to Sack (*Chem. Zeit.*, 1903, Rep., p. 148), the Chemische Fabrik Knoll & Co., of Ludwigshafen, sells a "purified tar," entirely free from free carbon, in appearance like olive oil, for medicinal purposes; it is stated to be specially adapted for the treatment of skin diseases, on account of the absence of pitch. The product is called "Anthrisol."

Joseph Giraud deodorizes tar or tar-oils for the manufacture of soap, etc., by heating with ammoniacal copper solution or by salts of iron, manganese, or chromium, adding an alkali and passing steam through the mixture.

Tixier (Ger. P. 138764) obtains all the soluble "extractive substances" contained in tar in a single operation as follows. A mixture of tar and sodium carbonate, corresponding to its percentage of soluble substances, is heated at a temperature between 60° and 100° C. The quantity of  $\text{Na}_2\text{CO}_3$ , as well as the most suitable temperature, is ascertained by previous trials. The mass gets into a state of frothing, the end of which shows that the reaction is over. Now a quantity of cold water, sufficient for dissolving the soluble portions is added and the solution decanted. By means of an acid the substances are precipitated, and mixed with the necessary quantity of sodium carbonate at 60° to 100° C. This produces a pasty extract, soluble in water, which can be brought into a solid form or into solution in the usual manner, and is used for antiseptic purposes in medicine.

Mann (Ger. P. 170133) dissolves such substances in a suitable volatile solvent, and pours that solution into a mixture containing both soap and some organic or inorganic colloid substance, *e.g.* starch. This mixture is heated and thoroughly stirred up, *e.g.*, by means of a steam-jet. When running the solution, say, of asphalt in benzol, into the hot mixture, the benzol volatilizes and is recovered by condensation; the asphalt, etc., remains behind, intimately mixed with the liquid, and remains in this state, if the agitation continues until the mass

has cooled down. If necessary, more water is added during this process, always with energetic oxidation. In this way an emulsion is obtained like an unguent, which mixes quite uniformly with water and forms a durable emulsion.

*Coal-tar for Denaturing Alcohol.*

Hache (Ger. P. 144485) mixes decanted tar with its own volume of spirits of wine, separates the liquid from the sediment, dissolves it in 1 to 10 parts benzol, and employs 1 part of it for 100 spirit of wine.

*Coke from Tar.*

Dahmen and Haggi Ristic (B. P. 20967, 1903) introduce tar in a thin jet into white-hot iron retorts, where it is decomposed with deposition of coke.

The manufacture of *soot* and *lamp-black*, for which sometimes raw coal-tar is employed, will be described in Chapter VIII.

## CHAPTER V

### THE FIRST DISTILLATION OF COAL-TAR

#### *Historical Notes.*

IT has been mentioned more than once in the preceding chapters that the utilization of tar by distillation is a comparatively new industry; but it had long been known that useful products could be obtained by that operation. In this respect a patent awarded to Henry Haskins, 7th August 1746 (*i.e.*, half a century before the first introduction of gas-lighting), is so remarkable that we quote it verbatim, as follows:—

“New method of extracting a spirit or oil out of tar, and by the same process produce the finest of pitch.

“First, take any quantity of tar you please, so as not to more than half fill your still, which must be thoroughly cleaned from all manner of impurities, and more particularly from water; for if any quantity of that should be left in it, it will be found to be exceedingly troublesome and considerably hinder the operation.

“The tar may be cleansed either by boiling or straining, or by settling in tubs, or any other convenient vessel; then commit it to a double-necked pelican-headed still, made either of glass, iron, or copper, with capacious receivers, and well luted, under which raise a fire of the first degree for six hours, by which time the particles will be thoroughly comminuted; then raise your fire to the second degree for as many hours more, and then to the third degree for three hours more, in which time you will find first a pale acid phlegm to come off into the receiver, which must be changed, when a fetid volatile oil or spirit rises; lastly will come over a black glutinous oil, which keep for use.

“If you would have a more volatile or light oil, which may

be more proper for many uses in physic, it may be done by many repeated rectifications to what degree you choose.

"Lastly, the caput mortuum, which is what remains in the still after the distillation is finished, will be found the finest and best of pitch, which I am well assured of, not only from my own judgment, but by the experience and testimony of many who have used it."

It is quite possible that in this patent wood-tar is meant, which at that time was much better known than coal-tar; but the principles of the distillation of the latter appear quite clearly in that old patent.

We have seen (on p. 19) that Accum, in 1815, was the first to boil down coal-tar in closed vessels (stills), and thus to obtain a volatile oil which could be employed as a cheap substitute for spirits of turpentine.

According to Dr Longstaffe (*Proc. Soc. Chem. Ind.*, 1881, p. 13), the first coal-tar distillery was erected by himself and Dr Dalston, near Leith, in 1822; the spirits went to Mr Mackintosh for waterproofing, and the residue was consumed for the purpose of making lampblack.

Roscoe<sup>1</sup> mentions that, about the year 1834, at the time when Mitscherlich had converted benzene (from benzoic acid) into nitrobenzene, the distillation of coal-tar was carried out on a large scale in the neighbourhood of Manchester; the naphtha obtained was employed for the purpose of dissolving the residual pitch, and thus getting black varnish. Attempts were made to supplant the naphtha obtained from wood-tar, which at that time was much used in the hat factories at Gorton, near Manchester, for the preparation of "lacquer," by coal-tar naphtha. The substitute, however, did not answer, as the impure naphtha left on evaporation so unpleasant a smell that the workmen refused to employ it. It was also known, about the year 1838, that wood-naphtha contained oxygen, whilst that from coal-tar did not; and hence Mr John Dale attempted to convert the latter into the former, or into some similar substance. When trying, for his purpose, a mixture of sulphuric acid and potassium nitrate, he obtained a liquid possessing the smell of bitter-almond oil, the properties of which he did not further investigate. This was, however, done

<sup>1</sup> Discourse at the Royal Institution, 16th April 1886, p. 4.

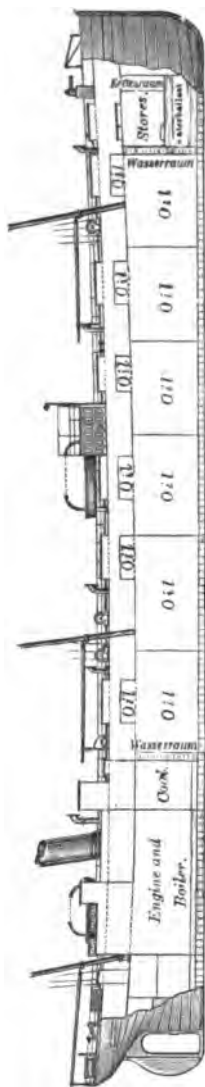


FIG. 71.

in 1842 by Mr John Leigh, who exhibited considerable quantities of benzene, nitrobenzene, and dinitrobenzene to the Chemical Section of the British Association meeting that year in Manchester. His communication is, however, so printed in the Report that it is not possible, from the description, to identify the bodies in question; and hence Leigh's merits in that respect were completely overlooked until quite recently.

The further steps in distilling coal-tar and utilizing the products therefrom, made by Bethell, Brönnner, and Mansfield, have already been noticed (pp. 20 *et seq.* and pp. 225 *et seq.*), and from that time dates the establishment of tar-distilling on a really large scale.

#### *Carriage and Storage of Coal-tar.*

Various descriptions of vessels are used for carrying the tar from the gas-works to the distilleries, according to the circumstances of the case. In England water-carriage is preferred whenever it is practicable, the canal-boats being constructed as floating tanks, with a cabin for the crew, which serves also as an air-space for augmenting the carrying-power. Such boats (Figs. 70 and 71) hold up to 250 tons of tar. On the Continent this is rarely possible; there the tar is usually carried by railway, in cylindrical or angular iron tanks fixed on a platform running on wheels (Figs. 72 and 73) and holding up to 20,000 tons of tar. If these tanks are made of pretty strong iron, they can be steamed out whenever the tar has become too thick, which may happen in winter. In Germany they are frequently provided

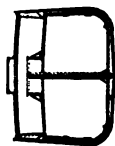


FIG. 70.

with coils of heating-tubes, connected with the steam-heating system of the railway-train. Angular (box-shaped) cisterns are more easily got at and cleaned inside; they hold about

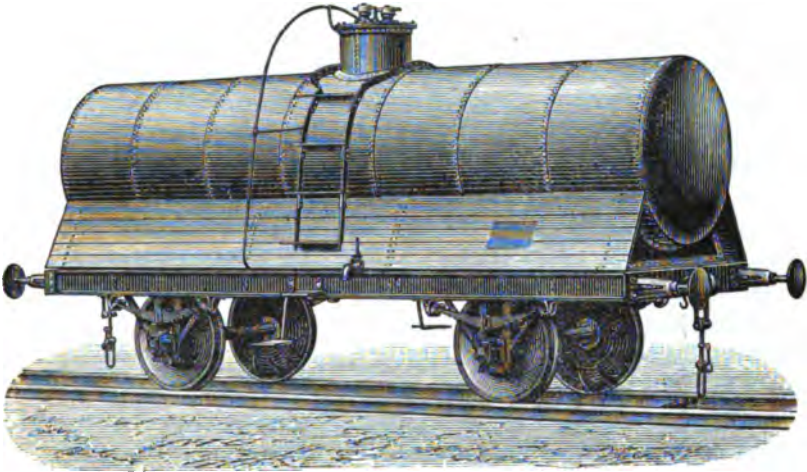


FIG. 72.

10 to 15 tons, a truck with two cylinders about 9 tons of tar. It is convenient if they are provided at the top with a pretty large pan serving in filling the tank, and with a movable crane for lifting up the full casks and lowering the empties.



FIG. 73.

Tar-barges or tank-wagons ought to be air-tight, so as to obviate the escape of effluvia (principally sulphide of ammonium) during the transit. While pumping, the cover should only be opened just sufficient for the pipe to pass in.



The tank-wagons for railroad traffic must, of course, be constructed in the fashion required by the railway companies, and provided with breaks.

In Paris (and elsewhere) tar is carried in iron or wooden casks resting on axles and drawn by horses, or, wherever possible, laid on railway-trucks. In Lancashire it is usual to employ wooden barrels (preferably of ash-wood), holding from 250 to 300 gall., resting by means of concave wooden bearers upon two-wheeled carts. The middle bearer rests just over the axle; and the barrel can be tipped behind, two iron adjustments attached to the back bearer preventing it from slipping down. There is a running-off cock of 2- or 2½-in. bore, and a charging-hole 4 or 5 in. square and closed by a wooden plug. Long barrels are said to be pulled more easily than those more bulged. A barrel costs about £3, the cart pertaining to it £14.

Rispler (*Chem. Zeit.*, 1910, p. 549) gives a detailed description of the arrangements for carrying tar and tar-products. In countries possessing ample waterways, the carriage of tar on these is considerably cheaper than by railway cisterns. In England, Belgium, Holland, and France the transportation of tar in tank-steamers is allowed, but not in Germany, in which country, therefore, the tar must be put into boats drawn by a steam-boat. The tank-boats hold up to 250 tons, or even more. They are built entirely of iron or steel, with several partition walls forming oil-tight compartments, and with cabins for the attendants.

From the canal-boats or railroad-trucks the tar is frequently pumped by steam-pumps into iron *store-tanks*, situated high enough for the tar, after the water has separated, to be run into the stills by natural fall. In Paris the draw-off cocks of the cylindrical iron store-tanks, which rest on high pillars, unite into a common main, which descends to the ground, runs underneath along the whole set of tar-stills, and gives off an upright supply-pipe with slide-valve for each still, by which these can be filled as required, by means of hydrostatic pressure, from the store-cylinders. Körting (*Stein- und Braunkohle*, 1909, p. 5) describes a convenient shape of such highly placed store-tanks for tar and ammoniacal liquor.

In other cases the tar, especially when it arrives in casks

is emptied into larger store-cisterns sunk in the ground (*wells*), and pumped from these either into the above-mentioned high tanks or directly into the stills.

Such underground tar-wells (also those for ammoniacal liquor) are frequently of very large dimensions, up to 60 ft. diameter (Watson Smith), since tar-distillers are generally bound by contract to rid the gas-works of their tar and ammoniacal liquor, which in the event of stoppages of business, accidents to the plant, etc., might cause them considerable embarrassment. On the other hand, if there is large storage room, a good stock may be collected in winter, when the gas-works are busiest, so that even in summer the stills can be regularly employed (Watson Smith).

Underground wells are not often made of iron, this being too costly and subject to corrosion. Usually they are made of brickwork set in cement, of a circular shape, secured underneath and round the sides by clay puddle. First the necessary excavation is made; then a good puddle is laid down on the bottom, completely levelled, and a double floor of bricks in cement laid on, the joints crossing each other. Now the sides are raised, likewise in double courses and hence 9 in. thick, leaving between the brickwork and the soil (in case of need kept back by wooden stays) a space of 8 or 12 in., which is filled in with puddled clay. The best method of proceeding is to complete each time a ring of about 4 ft. high, puddle behind it, and continue the walling. It is best not to work too fast, so that the brickwork may have time to settle; cracks once formed can hardly ever be repaired (Watson Smith).

Tanks made by the Monier system (cement concrete with a core of wire-netting) are said to be much cheaper and quite as good as brick tanks; they can be placed either below or above ground.

According to *J. Gas Lighting*, 1909, p. 808, tanks made of cement concrete, etc., are only tight against ordinary gas-tar, but not against water-gas tar.

The tar-wells are tightly covered with planks, to keep out the rain, etc. At the place where the carts are tipped there is a strainer with many  $\frac{1}{2}$ -in. holes and with sides and back, so that any bits of wood which might choke the pumps are kept back (Watson Smith). Or else all the carts discharge their contents

into a large spout, provided with outlets for each cistern (if there are several).

The tight covering-in of the tar-cisterns also avoids any nuisance from offensive gases whilst running in the tar. For this purpose the air driven out by the tar is made to pass through a box containing hydrated oxide of iron, which absorbs any hydrogen sulphide escaping (*cf.* later on the various plans for dealing with the noxious gases).

*Explosions.*—According to the Thirty-fifth and Thirty-sixth Annual Report of the Chief Inspector of Chemical Factories in England, not less than seven explosions of tar reservoirs occurred in the year 1885. On pumping the tar out of the cisterns, air enters these, and with the gases lying above the tar (hydrogen sulphide and light hydrocarbons) forms an explosive mixture which may accidentally take fire and cause destruction. According to Köhler, such observations have not yet (up to 1912) been reported from German tar-works, coke-works, or gas-works.

The *pumping of the tar into the stills* was formerly always done by ordinary pumps, specially constructed for thick liquids, and provided with a strainer at the suction-pipe to prevent choking up by chips of wood or the like. It was formerly assumed that such a thick liquid could not be raised by compressed air. This is, however, nowadays actually done at all the larger German works. Previously warmed-up tar can be pumped into the stills by means of air compressed to 28 lb. per square inch in half the time as with a good ram-pump.

Since most of the large tar-distilleries nowadays are working with application of a *vacuum*, it has also been attempted to charge the evacuated stills direct from the tar-pit by means of a rising-pipe. But this procedure, as shown by experience, causes the charging of the stills to take more time than when using a pressure-vessel, and the controlling of the proper fitting of the stills is more difficult. Hence that system has been pretty generally abandoned.

The *pumping by compressed air* is effected by placing a pressure-vessel (usually an old steam-boiler) beside and a little below the tar-reservoir, and connecting them (for large stills) by an 8-in. pipe and valve. This vessel should hold either half or the whole contents of a still. It is connected with the still by a

5- or 6-in. wide iron pipe, rising to the same height as the level of the tar in the still when full, with a valve just outside the still. This allows of providing for the frothing-up of the tar, by reconducting the rising tar into the pressure-vessel (see below). A removable strainer is placed just before the pipe connecting the reservoir with the pressure-vessel. If, in spite of this, the valve becomes choked up, it is easily freed again by admitting compressed air from the pressure-vessel into the tar-reservoir. A pressure-vessel holding 15 or 20 tons is filled from the reservoir in ten or fifteen minutes, and, with air compressed to 28 or 35 lb. per square foot, its contents are pumped up 15 or 16 ft. high in an hour or an hour and a half, more or less quickly in connection with the fluidity of the tar.

#### DISTILLATION BY STEAM.

The manufacture of coal-tar products begins by fractionally distilling the tar, mostly by a naked fire, but in some places or for special purposes by means of *steam* or superheated water. This plan is now very little used at large works—except in Scotland, where it appears to be general. Its advantage is only apparent where the tar has merely to be dehydrated and deprived of its most volatile constituents in order to employ the remainder (95 per cent.) for painting, for impregnating stones or roofing-tiles, or for the manufacture of roofing-felt (*cf.* pp. 353 *et seq.*). In such cases much trouble and danger of fire is avoided by substituting steam for a naked fire. The steam can be applied indirectly, as "*dry steam*," by surrounding the still with a jacket, or by means of a coil in which the steam circulates inside the vessel and issues again to the outside. In the outlet it is expedient to fix an apparatus for automatically discharging the condensed water, without allowing any steam to escape, of which apparatus many varieties are now made. The still may be of almost any shape; perhaps the best is an upright cylinder. The escaping vapours are condensed in a leaden or iron worm and separate in the receiver into ammonia-water and light oil, which is mostly sent to the larger tar-distillers for rectification.

It was formerly more usual, but is nowadays hardly done in well-conducted factories, to employ "*wet*" steam, directly blown

into the still, *e.g.*, by means of a coil of pipes lying on the bottom and perforated with many holes. According to Ure, such stills hold from 800 to 1500 gall., and the distillation is carried on till the specific gravity of the distillate has reached 0.910. According to Mills,<sup>1</sup> the stills hold from 500 to 4000 gall., and are horizontal cylinders; the steam brings over up to 10 per cent. of light naphtha (sp. gr. 0.78 to 0.83) and some ammoniacal liquor. The residue is run into cisterns, where tar and water separate. The "boiled tar" is now ready for the above-mentioned purposes, or can be run while hot into other stills for distilling by naked fire, which was formerly the usual course followed in Scotland. But this process is not advantageous, because there remains very much water with the tar, which can only be separated from it by being allowed to settle for some time; hence if a naked fire is to be used, it is best to do so from the first.

Sometimes the "boiled tar," resulting from the first distillation, is not discharged into a tank, but is pumped out through a pipe from the steam-still into a second still, heated by an ordinary fire, so as to avoid any exposure of the hot tar to the air and the evolution of disagreeable fumes.

The condensation of the escaping steam and naphtha-vapour, owing to the large quantity of the former, is rather more troublesome than when the distillation is effected by "dry" steam or by a fire. There is much more cooling needed, *i.e.*, longer worms and more cooling-water. The condensing mixture of naphtha and water divides at once into these two constituents, which can be kept apart by overflow vessels, as will be mentioned hereafter in describing the rectification by steam of the lightest oils (Chapter XI.).

The usual yield of naphtha by this plan is 2 to 6 per cent. from ordinary tar, or 10 to 20 per cent. from cannel-coal tar. The longer the operation is continued, the more, but heavier, naphtha is obtained.

The *naphtha* obtained by steam distillation is of course richer in volatile constituents than that obtained by direct distillation of tar. But it is far from containing only such constituents as boil at and below the temperature of the blown-in steam (rarely above 150° C.); a number of much higher-

<sup>1</sup> *Destructive Distillation*, p. 23.

boiling substances are carried along, as shown by the following analyses<sup>1</sup>:—

	I.	II.	III.
Oils up to 100° C. .	20.9	14.2	23.3 per cent.
„ 130° . .	5.9	13.2	8.0 „
„ 160° . .	8.7	19.6	15.2 „
„ 202° . .	16.0	16.6	23.9 „
Oils boiling above 202° (by difference) .	48.5	36.4	29.6 „
			Sp. gr.
I. Naphtha from the tar of the Hamburg		gas-works,	0.964
II. „ „ „ Berlin English		gas-works,	0.947
III. „ „ „ „ Corporation		gas-works,	0.932

Hence this product is not nearly so valuable as the “first-runings” of distillation over a naked fire, and is more similar to the “light oil” of that operation.

Köhler (*Z. angew. Chem.*, 1888, p. 677) has shown by practical trials that the boiling-over is less connected with the water contained in the tar than with its contents of “free carbon.”

In Scotland,<sup>2</sup> instead of distilling by steam, sometimes a fifth of its bulk of water is added to the tar and the whole distilled by a direct fire. Less but better naphtha than by steam distillation is said to be thus obtained. This process comes to the same thing as distilling by steam of ordinary atmospheric pressure, but does not seem worthy of recommendation, as the danger of boiling-over is very great.

#### DISTILLATION BY FIRE.

The more usual way of distilling tar, by a direct fire, has for its primary object the removal of the non-volatile or too-little volatile constituents, which form the greater portion of tar, in the shape of pitch, and to effect a preliminary fractionation of the distillates, which are then worked up singly. It is evident that this can be done only by a direct fire, since the boiling-point of the most valuable product from tar, anthracene, coincides with that of mercury (360°).

<sup>1</sup> From Kerl-Stohmann's *Chemie*, 3rd ed., vi., p. 1172.

<sup>2</sup> Ronald and Richardson, *Chemical Technology*, vol. i., p. 733; Mills, *loc. cit.*, p. 23.

*Operations. Dehydration of the Tar.*

The first condition of a quiet regular distillation is that the tar should be freed as much as possible from the ammoniacal liquor which is always mixed with it to a certain extent, and the presence of which is a disturbing element in the distillation. (The estimation of the water contained in the tar will be described at the close of this chapter.) So long as water and tar-oils boil at the same time, there is always a tendency of the liquid to "bump," or even to be jerked over explosively. This can be overcome by very cautious, slow firing; but shortening this stage of the work is certainly desirable, although it is hardly possible to do without it altogether. Hence *previous dehydration* of the tar is decidedly advisable whenever it can be done without too much trouble.

*Dehydration of the tar by settling at ordinary temperatures.—*

If the tar be sufficiently fluid, mere prolonged rest will separate a large portion of the ammoniacal water from it; for as the water is only mechanically suspended in the tar and is of less specific gravity, it will rise to the surface, whence it can be drawn or ladled off. Preferably very tough tar is mixed with thinner tar to facilitate the separation of the water. In many places nothing else is done for this purpose but storing the tar in several large cisterns, holding, if possible, several hundreds of tons each, which are best placed at such an elevation that the tar can be run from them straight into the stills. Whilst one of these cisterns is being filled by pumping in fresh tar, the others are allowed to rest; and from that which has stood longest the now somewhat dehydrated tar is drawn off.<sup>1</sup> In this way the water contents of the tar may be brought down to 4 or 5 per cent. In Germany this is the maximum percentage of water tolerated in the tar purchased from the gas-works and coke-works. Any excess of water over the above-mentioned limit is deducted from the price to be paid for the tar. At some factories a closed steam-coil is laid in the cisterns, by means of which the tar can be heated at will, in order to make it more fluid and to separate the water

<sup>1</sup> According to Watson Smith, at small works tar and gas-liquor are allowed to settle in the same tank; the tar is drawn off by a tap in the bottom, the ammoniacal liquor by one placed higher up, into their respective stills.

better. In summer there is no occasion for this; but in the colder seasons the tar is heated to  $20^{\circ}$  or  $21^{\circ}$ , sometimes up to  $40^{\circ}$ . Hardly any perceptible loss of benzol occurs at this temperature, as there is a layer of water on the top of the tar.

A more complete separation of tar and ammonia is aimed at by the invention of J. and R. Dempster (B. P. 3245, 1882). To the opening, out of which the liquor or tar passes, a suitably-shaped box is fixed, having a vertical pipe screwed therein, with an overflow cup on the top, which can be raised and lowered by means of a screw to suit the height of liquor in the vessel, so that it can flow over the edge of the cup down the screwed pipe into the box, and out at the outlet.



FIG. 74.



FIG. 75.

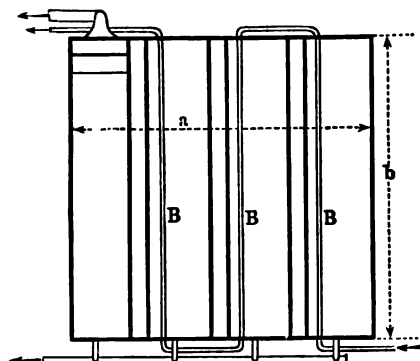


FIG. 76.

In Germany a number of gas-works employ Kunath's separator, as supplied by the Berlin-Anhalt Engineering Company (Ger. P. 15255) (Figs. 74, 75, 76). The principle of this apparatus is to spread the tar on broad overflow-spouts. The tar, slightly heated by means of the steam-pipes B B, on running over the spouts A A, separates from the water. This separation is further promoted in the vessels I., II., III., IV. by the water overflowing near the top by the lateral pipes, whilst the tar passes on at the bottom in the direction indicated in No. 1 by the arrow, and is carried on to the top of the next-following vessel. The outlet of the water in vessel I. is situated so much higher than the spout A in the vessel II., that the difference in height corresponds to the difference in specific gravity between tar and water. There are 7 sizes of this



apparatus, for separating from 1000 up to 8000 litres (225 to 1777 gall.) per twelve hours.

Similar apparatus have been described by Ruppert (Ger. P. 40204); by Krayenbühl, Peterson, and Burmeister (B. P. 15067, of 1887); by Öttner (Ger. P. 210590); by Klönne (Ger. P. 196240).

At smaller works Schlosser's *tar-separator* (*J. Gasbeleucht.*, 1902, p. 923) may do good service. The tar is put into a tank, placed on a cylinder with horizontally corrugated sides, and is allowed to flow over. In running over the corrugations, the separation of the water and tar takes place more easily, and both are collected in a table below.

A similar principle appears in the process of the *Deutsche Continental-Gasgesellschaft Dessau* (Ger. P. 191432). The tar is conducted downwards in an open spout, inclined at an angle of  $45^\circ$  against the horizon, to a point underneath the level of the liquid in a collecting-tank, in such manner that the tar, while flowing down in the spout, remains below the water flowing on its surface, and just the same also below the surface of the ammonia water already contained in the collecting-tank, until it reaches the level of the tar already separated in the latter.

*Dehydration of the tar by centrifugalling.*—By this method the tar can be very efficiently deprived of water down to 1 per cent., so that, according to Menzel (*J. Gasbeleucht.*, 1902, p. 467), it becomes immediately fit for the manufacture of roofing-felt. According to the *J. Gas Lighting*, 1908, p. 487, this is done at an expense of 6d. to 1s. per ton of tar, if carried out in the following way, in the apparatus shown in Fig. 77. The tar is heated up in a special vessel to  $40^\circ$  to  $50^\circ$  C., and is run through pipe F into the rapidly revolving drum of the centrifugal. The tar, being heavier, goes to the periphery of the drum; the water being lighter, separates more inside. The top part of the drum is, by means of suspended ring, separated into an upper and lower compartment. The tar goes to the top through the space left between this ring and the mantle of the centrifugal and leaves it through pipe A; the water runs off through pipe B. Any solid impurities stick to the drum and are from time to time removed.

Some gas-works effect the dehydration of the tar by this

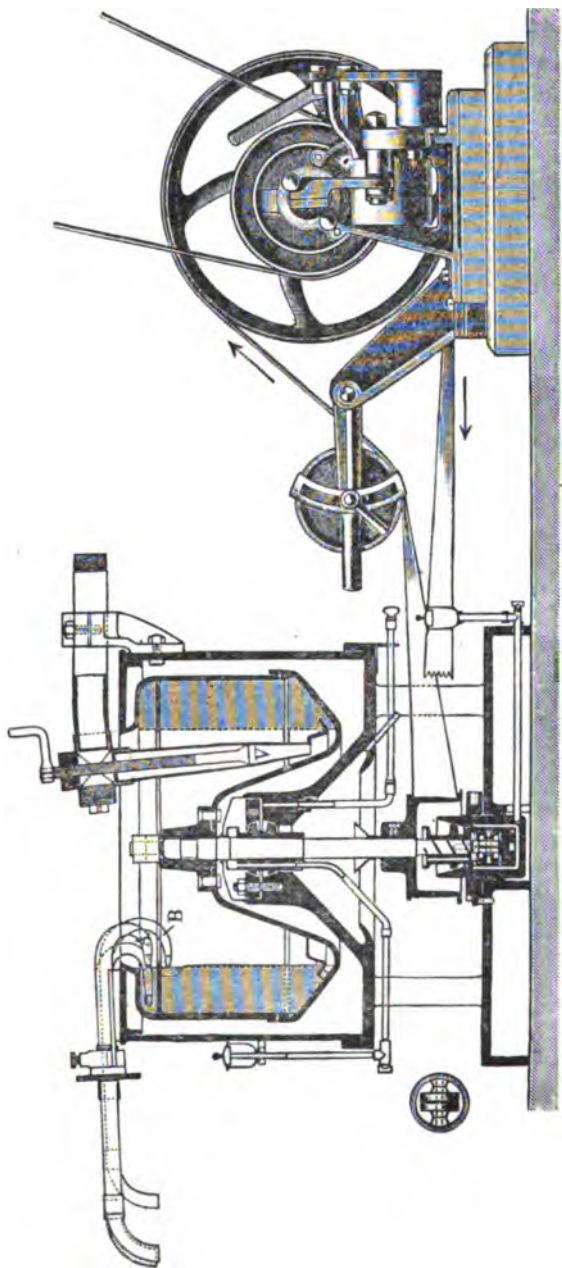


FIG. 77.

process, and obtain a better price for this tar than for raw tar, apart from the saving in freight. For large gas-works, which work up their own ammoniacal liquor, that method also allows of a more complete recovery of the ammonia.

The dehydration of *water-gas tar* by centrifugalling is not a matter of course, as the specific gravity of water-gas tar is very near that of water, viz., from 0.99 to 1.04, and there are such tars of exactly the same specific gravity as water itself, viz., 1.00. J. M. Müller (*J. Gasbeleucht.*, 1912, p. 229) has, however, succeeded in dehydrating even such tar by centrifugalling in the following manner. The expansion coefficient of water-gas tar by changes of temperature differs pretty strongly from that of water; if such tar of sp. gr. 1.00 is made from 15° to 20° warmer or cooler than the water, the difference between their specific gravities is sufficient for allowing their separation in the centrifugal. In his experiments the tar was heated up to 70° or 80° by means of exhaust steam, and put into a centrifugal making 2400 revolutions per minute, whereby a complete separation was effected into clear water, dehydrated tar of excellent quality, and solid residue, the latter adhering as a consistent mass to the inside of the drum. In a special instance there was obtained 17 per cent. of water, nearly 91 per cent. anhydrous tar, and 2.6 solid residue. By this process about 2 tons of tar can be dehydrated *per diem*.

*Dehydration of the tar by heat.*—As a matter of course, the separation of water and tar goes on all the more rapidly and completely the *thinner* and less viscous the tar is, and this is most thoroughly effected by moderately *heating it*, which to a certain extent also splits off the *chemically* combined water. This can be done to a certain extent even in an open tank or vessel, as mentioned above, but it is effected more thoroughly at a higher temperature and in such manner that the escaping vapours are condensed to a mixture (easily separating) of light oils and ammonia water. For this purpose the following apparatus have been constructed.

According to Girard and Delaire,<sup>1</sup> the dehydration of tar is effected by heating to from 80° to 90° in large boilers, by means of a steam-coil or jacket, or by a direct fire. The volatilizing oils

<sup>1</sup> *Dérives de la Houille*, p. 7.

are condensed. After from twenty to thirty hours the separation of tar and water is sufficiently complete, so that the water collecting at the bottom (?) of the boiler can be drawn off by a cock. The tar is now charged hot into the stills. If this description were correct, it would be precisely similar to the process described on p. 381; only it is called a dehydration instead of a distillation, as we have (assuredly more correctly) called it. But we have already stated that a division of the distilling-process into two phases, by steam and by direct fire, whether it be theoretically correct or not, does not seem to have stood the test of practical experience, for none of the largest works proceed in this manner. Girard and Delaire's description is evidently at fault in that it makes the water collect *below* the tar, which is impossible in the case of coal-tar. The same error is committed by Bolley,<sup>1</sup> undoubtedly owing to a confusion between coal-tar and lignite-tar, etc. In consequence of a similar inconceivable confusion, C. Vincent<sup>2</sup> states the specific gravity of *coal-tar* as 0.85 or 0.94!

A very efficient method of dehydrating the tar is the following, practised at one of the largest and best German tar-distilleries as the commencement of the distillation-process itself. The tar is pumped as it is into the (very large) stills until it begins to run out of a small overflow-cock placed just below the upper dome of the still, whereupon the pumping ceases and the firing is started. Before the tar arrives at the boiling-point, it has, of course, turned quite thin, and most of the water has collected on its surface. But as by the heating the bulk of the liquid is increased and its level rises above that of the overflow-cock, the watery portion can be drawn off by opening that cock from time to time. Even if a little tar should escape with the water, no harm is done. Whatever vapours are given off during this heating must pass on to the condensing-apparatus, and are thus utilized.

According to a communication, received from Dr G. Kraemer in 1907, the method then usually practised in Germany is this. A still is half-filled with tar and this is heated to boiling. The vapours pass through a short column fed with fresh tar, which is thus dehydrated and arrives in the still freed

<sup>1</sup> *Chemische Technologie der Gespinnstfasern*, p. 27.

<sup>2</sup> Payen's *Précis de Chimie industrielle*, 1878, ii., p. 944.

from water. From the still it flows continuously by means of an overflow siphon into a reservoir from which the ordinary stills are fed.

A special dehydrating still, "alambic à circulation," has been patented by Th. Foucault (supplied by L. Poillon, 158 Boulevard Montparnasse, Paris). Figs. 78 and 79 show its construction. It is a rectangular box (A), heated only at one side, and divided into two unequal parts by a perpendicular partition (C), also by a slanting plate (B). The cover is formed by an inverted pyramid (K), in which circulates cold water, introduced through I, and running out at T; a gutter (F) receives the liquid condensing from the vapour upon the lower side of K. The tar is introduced through J, and at first takes its level in both compartments, as regulated by the tap E. As it is heated in the smaller compartment alone, it swells up there, rises, and at last gets up to the slanting plate B, on which it spreads out, is cooled down, and runs back into the larger compartment, whence it flows back into the smaller compartment, where it again swells up and overflows on to B, so long as any water is present. The vapours of steam and light oil which are formed condense, on touching the cooled cover, into a liquid, which falls into the gutter F, and is carried out of the still by the siphon-tube G; the gases escape through H. After some time the circulation becomes slower; the tar ceases to froth and swell and becomes hotter. It is now perfectly quiet, and can be run off through D and P into the ordinary stills, where it is now distilled without any bumping or dangers.

The Rütgerswerke A. G. (Ger. P. 161524) dehydrate coal-tar by heating from the top downwards, first the steam-space, then the upper portion of the liquid, formed of the water floating on the top, then the lower portion, holding water in emulsion, and lastly removing the chemically combined water. Two (or three) stills are working in a set. The waste fire-gases from the lower stills are conducted first round the steam-space of the top still which serves as a dehydrater, and then circulate round the lower part of the same. The water is thus completely separated in the upper still, and the dehydrated tar which runs into the lower stills is distilled in these much more quickly than otherwise, without fear of boiling over.

Sommer has filed a patent application for the following

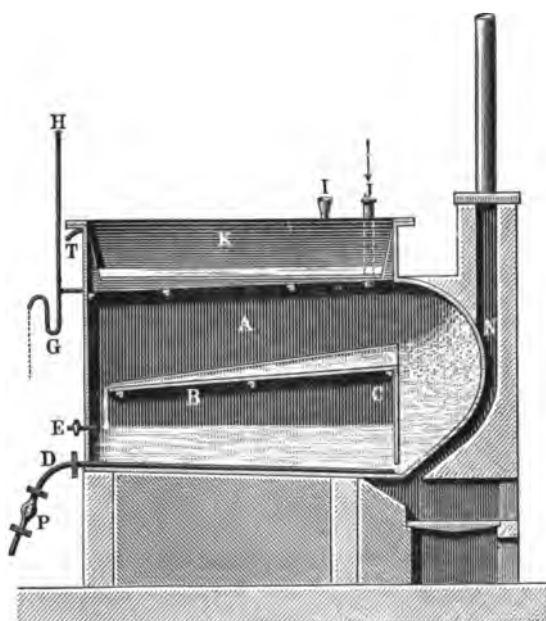


FIG. 78.

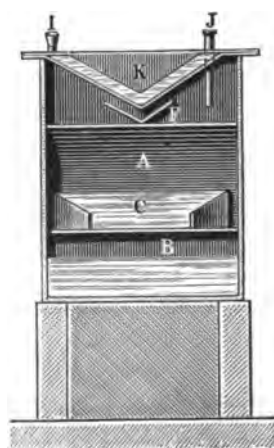


FIG. 79.

apparatus (Fig. 80) for separating the water from tar without danger of fire. The tar is boiled in pan *o* till free from water, then by overheating *o* it is driven over into pan *o'*, so that the lighter portions collect in *o'* and the heavier ones (pitch) remain in *o*, from which they are run from time to time. In order to drive the tar from *o* to *o'* without danger of fire, *o* is surrounded by a double wall (*c*), which prevents any overheating on the outside of the pan. Underneath *a* is an annular spray-pipe (*w, w*), fed from the tank *v* and instantly started by means of *w'* from without.

Klönne (Ger. P. 196240) dehydrates the tar by grinding it by means of heatable rollers. This liberates the particles of

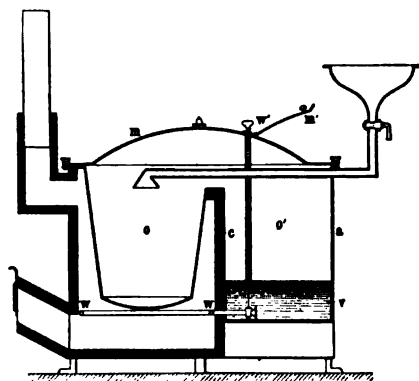


FIG. 80.

gas-liquor enclosed in the viscid tar, and produces tar, free from gas-liquor, more cheaply and conveniently than is possible by long storage, or heating, or centrifugalling. The same inventor (Ger. P. 192535) utilizes the vapours given out by the tar when being heated for the purpose of dehydration, by employing closed store-tanks provided with arrangements for heating and for condensing the vapours evolved.

Wilton (B. P. 26910, of 1907) first heats the tar under such pressure as will prevent boiling and frothing of the contained water, and then reduces the pressure so as to liberate the water in the form of steam, at such a temperature that the main volatile constituents of the tar are not liberated, and the tar, now free from water, can be distilled with ease. A small quantity of naphtha and ammonia passes over with the steam, when the

pressure is reduced, as explained, but these can be easily recovered by condensing the steam. Wilton's apparatus is supplied by the Chemical Engineering Co., and Wilton's Patent Furnaces Co., of London.

Other apparatus for dehydrating the tar by heat have been described by Chemische Fabrik Lindenhof, at Mannheim (Ger. Ps. 217659, 218710, of 1908); Soci  t   du Gaz de Paris (Fr. P. 402917, of 1909); C. H. K  hn and E. M  nster (Ger. P. appl. 4408, of 1910); Rispler (*Chem. Zeit.*, 1910, p. 261); Lemmer (Ger. P. 238013; *Z. angew. Chem.*, 1911, p. 1004). Taizo Kuroda (*J. Chem. Ind.*, Japan, 1915, p. 413); *Gas World*, lxii., No. 1602.

C. H. Webb (*J. Gas Lighting*, 1913, cxxiv., p. 505) describes the process of dehydrating tar for road-making, carried out at Stourbridge. It is heated under a pressure of about 2 atmospheres to 170   to 180  ; on reducing the pressure, water and light oils evaporate, and leave anhydrous tar behind. The raw tar is continuously pumped through a coil of pipes, surrounded by the hot, dehydrated tar into a still, where it is brought to the above-mentioned temperature; from this it flows through a reducing-valve into another still, where, in consequence of the sudden lowering of temperature, the water and the light oils evaporate and are condensed in a cooler. This process has the advantage against the heating of the tar in open vessels that the light oils are not lost.

The very disagreeable *frothing* during distillation of mixtures of tar and water, according to B. P. 707, of 1914, of Crossley, Wheeler, and Smith, is avoided by placing a horizontal pipe or superheater in the upper part of the still. This pipe is heated by a flame or hot flue-gases, considerably above 100  ; part of the froth is evaporated, and the remainder falls back into the still.

#### *Dehydration of Tar by Chemical Methods.*

Gutensohn (B. P. 21800, of 1908) avoids the danger of fire in the first phase of the distillation of tar, and the frothing over caused by water contained in the tar, at the same time obtaining a better quality of pitch, by treating the tar with a mixture of chromic acid and sulphuric acid. The heat produced by oxidation effects the distillation of benzol, etc., which is retained in a condensing-apparatus. When no more light



oils come over, the mixture of acids is run off, and the remaining thickened tar is distilled in the usual manner, which in this case requires a temperature lower by one-third than the old process. The pitch ultimately remaining is of very good quality, and is especially well adapted for rendering textile matters water-tight by impregnation, as it is somewhat elastic.

[This process is probably too expensive for practical execution.]

Scholvien (Ger. P. 161236; patented in the United Kingdom by Oppenheimer & Kent, B. P. 12696, 1903) dehydrates the tar by quicklime or anhydrous calcium sulphate (burnt plaster of Paris). This process is more especially intended for water-gas tar; in the case of ordinary coal-tar it will hardly come into use, for it would lead to a loss of phenols by the formation of calcium compounds. According to the German patent 163623, the tar dehydrated in this manner is distilled down to pitch. The distillate is treated with acid and alkali in the usual way and distilled again, thus obtaining in the first instance a perfectly limpid distillate, smelling faintly ethereal. When the distillate begins to show a yellow colour and oily appearance, it is caught separately, again treated with acid, and alkali, and redistilled. Thus a clear liquid is obtained, of specific gravity 0.860 to 0.920, boiling between 100 and 270° C., and consisting of hitherto unknown hydrocarbons. Its inflamm.-point is 30° C. above that of petroleum; it is specially adapted for motor engines, where it gives out 20 to 30 per cent. more power than ordinary distillates, and it can also be used as a substitute for oil of turpentine.

#### *Purification of the Tar from Free Carbon.*

The free carbon, always contained in coal-tar to a certain extent, is troublesome, especially through forming a deposit at the bottom of the still.

E. Jacobsen<sup>1</sup> proposes purifying the tar from carbon previously to its distillation. If coal-tar be mixed with half its volume of carbon disulphide, all the free carbon will separate as a powder; and if the liquid be decanted, the carbon disulphide blown off by steam, and the residue mixed

<sup>1</sup> *Chem. tech. Repertorium*, 1869, ii., p. 107.

with petroleum-spirit, all the brown asphalt will be left behind, whilst the remaining liquid, the petroleum-spirit having been steamed off, will consist of an orange-coloured clear oil containing naphthalene, anthracene, etc. Similarly, coal-tar pitch can be purified from its carbonaceous and asphalty portions; the hydrocarbons remaining over are more easily fractionated, and a smaller proportion is gasified on heating, so that anthracene can be recovered from them with more facility. Carbon disulphide and petroleum-spirit are easily recovered without any essential loss (?). When petroleum-spirit is added directly to coal-tar, the asphalt, which is precipitated, forms, with the free carbon and a portion of the dead oil, a tough, difficultly manageable mass; and by adding a mixture of carbon disulphide and petroleum-spirit, part of the brown asphalt is dissolved. Hence the process should be conducted exactly as above described. [I am not aware that this process has ever been carried out on a large scale: it seems too expensive and too dangerous as regards fire, and probably a good deal of anthracene will be left in the "free carbon" and the "brown asphalt"; neither would it be easy to re-obtain the dissolving-medium free of cost.]

Lennard (B. P. 2183, 1899) also proposes removing the free carbon before distilling the tar.

Gaster (B. P. 6739, 1901), for the purpose of removing the free carbon, first distils the tar as usual until a temperature of about 260° C. is reached. The distillation is then interrupted, and to the partially cooled pitch in the still naphtha is added, from 1 to 3 parts to 1 of pitch, in a mixing vessel provided with an outlet for the vapours formed to a condenser. The mixture is now either at once transferred to a heated retort, or after separation of part of the free carbon by settling or by a centrifugal. In the retort the volatile solvent and the heavy oil (pitch) are separated in the shape of vapours [?] from the free carbon, and are conducted to a cooling or pitch-collecting pot, where the heavy oils (pitch) are collected, and, if necessary, are mixed with other oils for obtaining the desired quality of the pitch. [I am not responsible for the apparent inconsistencies of this description, which in the patent specification goes on a good deal longer, without throwing more light on the above.]

Nikiforoff (Ger. P. 143549) employs a water-cooled tank

provided with a partition and a stirrer at the bottom of this. This tank is filled with tar. The products of dry distillation are forced through this, and here yield their free carbon to the tar; the temperature being kept at about  $170^{\circ}$ , everything volatile at that temperature escapes and is condensed in the usual manner.

Witt (*Chem. Ind.*, 1901, p. 326) reports on carbon-free coal-tar, exhibited in Paris, 1900, by Johan Ohlsson's Tekniska Fabrik, of Stockholm, a clear, transparent, brown fluid, the use of which he was not able to ascertain. The carbon, exhibited at the same time, had not the appearance of soot, but of graphite, and might probably serve much better than the "graphite" from gas-retorts for electric arc carbons, crucibles, etc. This process is again mentioned and recommended in *J. Gas Lighting*, cxiv., p. 835 (1911). [According to G. Kraemer, the iron present in such carbon obtained from tar by means of solvents is an obstacle to its use.]

O'Reilly (B. P. 22853, of 1908) has found that, if the tar is first warmed up to  $65^{\circ}$  to  $120^{\circ}$  and then exposed to pressure, either from above or producing a vacuum below the filter, the separation of the suspended matter can be carried out quickly and cheaply by purely mechanical means. The substance remaining on the filter is essentially free carbon, which can be employed as painters' colour, or for electrical purposes (electrodes, etc.). The tar passing through the filter can be employed for all the well-known purposes, or distilled in the usual manner. Its specific gravity (1.05 to 1.20) exceeds that of any tar-oil, and it is especially well adapted to the impregnation of wood, which the inventor describes in another patent (B. P. 22854, of 1908).

Lowry and Bernhard (U.S. P. 951993, 1910) heat the tar in a cylinder, the lower part of which is a chamber provided with a steam-coil, to about  $120^{\circ}$ , and filter it in a chamber at the top of the cylinder by means of discs, consisting of soft wood or any other filtering-medium into a spout surrounding the apparatus from the outside. The free carbon (which should be removed as completely as possible when employing the tar for the pickling of timber) remains behind in the shape of a muddy mass which is carried downwards by revolving scrapers and run off at the bottom.

The Rütgerswerke Aktiengesellschaft (Ger. P. 208600)

remove the free carbon from the tar or pitch, previously to its combustion for the manufacture of soot, by means of creosote oil or pitch, which on the one hand produces a better quality of the carbon, and on the other hand increases the yield of soot. A similar process is employed by Krojanker (Ger. P. 227492, 1909) for preparing an impregnating-oil, containing bitumen and stable in the cold, as will be further described in another place.

Specially for the manufacture of pitch from *blast-furnace tar*, Craig (B. P. 2943, 1907) prescribes to dehydrate the tar by heating, and then to treat it in a centrifugal separator, or to pass it through a filter-press, whereby from  $7\frac{1}{2}$  to 10 per cent. of "clayey" sludge, containing 50 to 66 per cent. of ash, is removed. The purified tar is subsequently distilled in the usual manner.

J. M. Müller has made experiments on removing the free carbon from gas-tar by centrifugal action; he succeeded in reducing it to a third of the original proportion.

#### *Construction of Tar-stills.*

Only one material is suitable for tar-stills, viz., *wrought-iron*. Cast-iron stills would be less subject to burn away and to mechanical injury in getting out the coke; but they cannot be easily made of considerable size. Both the difficulties and the cost of casting increase very rapidly with an increase in the size of hollow objects; neither can a perfect uniformity of structure be expected in the case of unusually large castings. Even when they are made as upright loam-castings and with a large feeding-head, an air-bubble may very easily remain, and, in the case of vessels exposed to a direct fire, cause in that place a most dangerous tendency to crack. But even a faultless casting is still very liable to crack, and must never be set without a curtain-arch over the fireplace: nevertheless any carelessness of the fireman will cause it to crack; and the mischief will then be great in proportion to the size of the vessel. Wrought-iron vessels, on the other hand, cannot be cracked by incautious firing, at least not in consequence of sudden changes of temperature, although an explosion from an excess of pressure, if all outlets are stopped up, is still possible.

It is true that the plates are more easily burnt by the first action of the fire than cast-iron; but this must, under any circumstances, be provided against by a curtain-arch. It takes very gross and long-continued carelessness on the part of a fireman to burn the plates of a properly set still, whilst even the best workman cannot always help the cracking of a cast-iron still.

It should be further noticed that the metal of cast-iron stills must be at least four times as thick as the usual boiler-plates; this makes the former much more expensive than the latter, and increases the consumption of fuel. Lastly, wrought-iron stills can be repaired by patching, or by putting in fresh plates, whilst similar repairs are nearly always excluded in the case of cast-iron.

Cast-iron is, however, the proper material for the still-head, the cooler, and other parts not exposed to the risk of cracking; it resists the action of the ammoniacal vapours better than wrought-iron. The connection between the still-head and the cooler is best made of wrought-iron, as this is tougher, and the risk of cracking through the changes of temperature is very great just in that part.

If wrought-iron stills are protected, by means of a "curtain-arch," from injury by the first heat of the fire, they last very long, provided they are properly treated, especially in cleaning out. A new still should go at least four years without any great repairs, and as long again after each thorough repair. The plates burn through most easily at the bottom, where the flame issues from underneath the curtain-arch, if the latter does not reach right through. Where this is the case, so that the still-bottom is not touched at all by the flame, and is only as it were in a hot-air bath, the stills may last much longer than the above-mentioned time.

Zmerzlikar (*Z. angew. Chem.*, 1893, p. 210) observed that the sheet-iron tar-stills working in the Rütgers factories, in Upper Silesia, showed strong corrosions in certain parts. Whilst some stills, made of Styrian sheet-iron, stood from 500 to 700 distillations, others became useless after a very few operations. The metal contained 0.04 per cent. phosphorus and 0.08 per cent. carbon, which cannot be faulty; a higher percentage of carbon cannot be exacted from the rolling-mills, since it would tend to make the plates brittle.

Stills worked only for soft pitch last, of course, much longer than those worked for hard pitch.

As curtain-arches, etc., cause more fuel to be consumed, some prefer doing without them, and strive to prevent damage to the still-bottom by frequent cleaning out. According to G. Kraemer (priv. comm.), long practice has proved to him that curtain-arches may be dispensed with if the stills are placed sufficiently high (3 to 6 ft.) above the fire-grate. *Cf. also infra* the statements of Rispler.

The following general rules should be observed in constructing wrought-iron stills:—The *thickness of the plate* of the sides as a rule need not be over  $\frac{3}{4}$  in.; the very greatest thickness, for 40 or 50 tons of tar, should be  $\frac{1}{2}$  in. The upper plates should be quite as thick as the lower plates, since they wear out rather more quickly (see below). The top and bottom are made rather thicker than the sides, especially where a vacuum is to be employed; in this case the top plates should be at least  $\frac{1}{2}$  in., the bottom plates  $\frac{3}{4}$  in. thick.

Of course the plates must be very well riveted and caulked; but in spite of that the seams of new stills often show a tendency to leak at the end of the distillation, when the temperature has risen very high. This is seen by a flame running along the seams or rivets; it always occurs at the bottom, and can be cured by fresh caulking. Even without that, coke soon sets into the seams and makes them tight; hence such leaking is mostly noticed after a thorough cleaning of the stills. In any case it does not endanger the safety of the still. The same thing holds good of the stills for light oil and other similar ones, to be mentioned hereafter.

Much difference of opinion exists as to the best *shape of a tar-still*. Formerly anything was made to answer, especially old steam-boilers of various shapes. Mostly this was bad economy; increased consumption of fuel, longer time of working off, frequent repairs, and frothing over of the contents of the still amounted to several times the cost of a new tar-still of the best pattern. But there is much dissension upon the question, What is the best shape of a tar-still? The following is a description of various forms of stills found at well-conducted works in different countries.

The form of still almost universally met with in England

and also at the majority of German works, is an *upright cylinder* of nearly equal height and diameter, with a dome-shaped top and a concave bottom, *i.e.*, equally curved upwards in a dome shape. This concave bottom is preferable to a flat bottom, on account of its greater stiffness and larger heating-surface, and because the iron can better expand and contract during the inevitable great changes of temperature to which it is exposed. Convex bottoms would have equal advantages, but would not present such a favourable proportion between the heating-surface and the contents of a boiler as concave bottoms; they are not so easily set, and the pitch could not very well be run out completely by means of a cock in a lateral direction.

Such stills are always made of considerable size, both to save labour for attendance and because the separation of the products according to their boiling-points is easier the larger the quantity treated in each operation. Rarely are smaller stills used than those for a 6-ton charge; but they are sometimes preferred because a charge can be worked off in ten or twelve hours, and night-work thus becomes unnecessary. But the large works usually have larger stills: in England, holding from 10 to 20 tons, rarely more; in Germany, 20, 25, or even 50 tons. It is doubtful whether such very large stills are the best; 20 tons seems the most convenient size; and more recently 15-ton stills have also been frequently erected in Germany. Some factories formerly working with 50-ton stills have recently gone back to 15- or 20-ton stills, which can be worked off within twelve hours, thus avoiding the risky night-work.

Figs. 81 and 82 show the shape of tar-stills of 18 tons capacity, according to Rispler, *Chem. Zeit.*, 1910, No. 51.

Watson Smith advises trying the tightness of every still by putting it on its seat, connecting it with a steam-boiler, closing all openings, and blowing in steam at  $2\frac{1}{2}$  atmospheres' pressure; it should not leak anywhere then. (Evidently an air-cock must be left open till all the air has been expelled.) He also observes that there is usually some difficulty in fixing the cast-iron still-head, inasmuch as the cover is mostly made of several pieces overlapping each other at the seams, and thus presenting obstacles to a tight joint with the flange of the still-head. This can be avoided, either by making the top piece out of one plate with a circular opening for the head; or else, if the top is

FIG. 81.

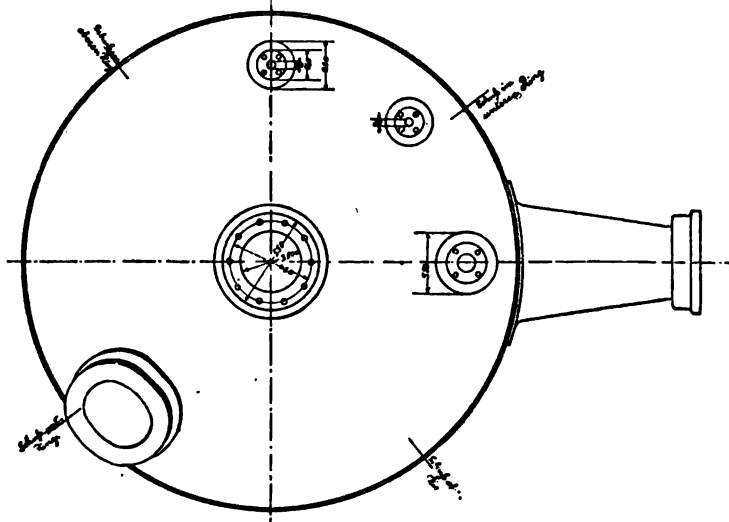
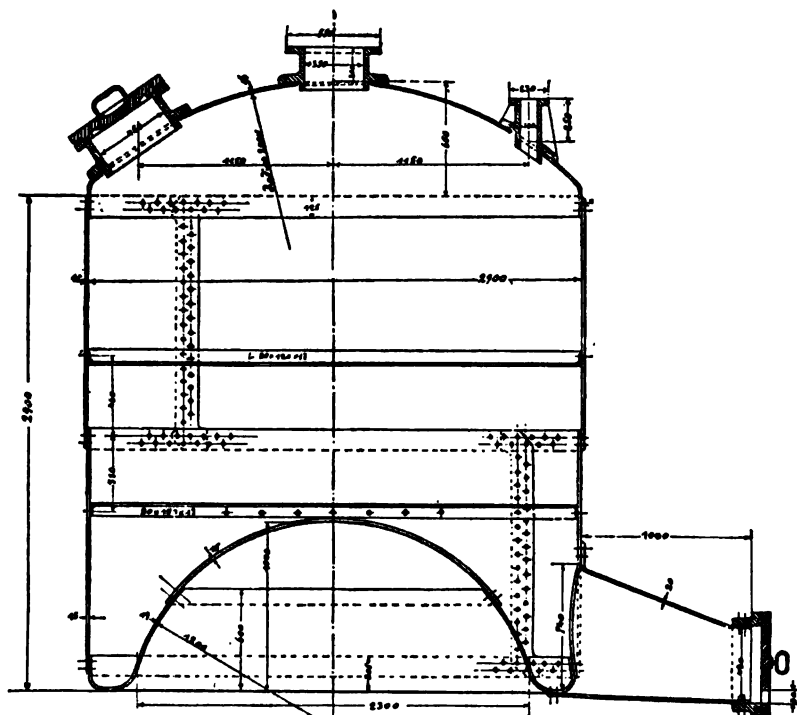


FIG. 82.



constructed of several pieces, by making a wrought-iron ring to fit the central opening (previously provided with rivet-holes), hammering it down while red-hot, so hot that it adapts itself to all the uneven places of the joints, marking the places for the rivets, taking the ring off, punching the rivet-holes, putting the ring on again, and riveting it fast to the top. The inner border

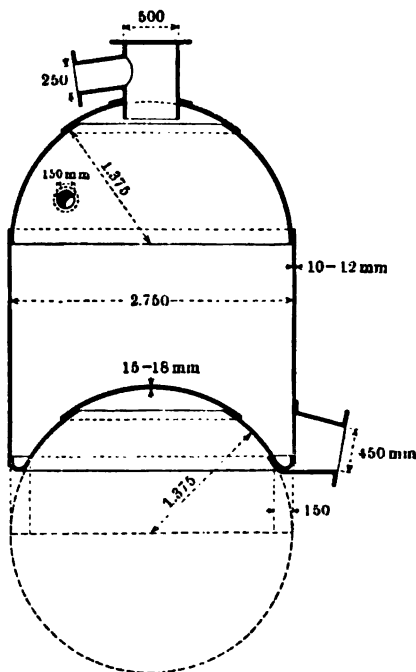


FIG. 83.

of this ring, projecting into the central opening and left quite smooth, serves for bolting on the still-head.

The German tar-distillers do not agree with all these assertions. In their opinion a high-pressure test is useless, as the stills are never subjected to such pressures, and the test itself might damage the stills; it is sufficient if the stills hold tight at 7 or 14 lb. pressure over that of the atmosphere. But the quality of the plate for making the bottom is all-important. If possible its breaking-strain should be tested before using the plates. The construction of the bottom, as shown in Fig. 83, is that of a semi-globe of the same diameter as that of the

cylindrical part; the edges are turned up and riveted to the cylinder shell. This turning-up makes the bottom more elastic, without sacrificing its strength, and it avoids the cuneiform space between the bottom and the cylindrical portion, which soon chokes up with coke, thus causing the iron to get red-hot and to burn through. In the case above shown the running-off tap can be fixed in such manner that all the pitch comes out.

Both bottom and top of the still are made in Germany of a central cap and four or five segments, joined by a double row of rivets; thus the difficulties mentioned by Watson Smith as to fixing the still-head are entirely avoided. Sometimes the bottoms even for stills of more than 8 ft. diameter are made of one piece; but these are less stiff than those made of several pieces.

Formerly the joints were made with the well-known rust-cement, or modifications of it. But asbestos board is far better than this, both for the flanges and the manhole lids, etc., for no kind of cement stands the strain put upon the joints by the expansion of the iron under the influence of heat.

The thickness of the plate differs according to whether it is for the top, the bottom, or the cylindrical part of the still. According to Warner (*J. Gas Lighting*, 1910, p. 132), the usual thickness in England is  $\frac{3}{8}$  to  $\frac{1}{2}$  in. for the cylindrical mantle,  $\frac{1}{8}$  to  $\frac{3}{4}$  in. for the bottom, and  $\frac{7}{16}$  to  $\frac{9}{16}$  in. for the top dome. In Germany the usual thickness of the plate for the cylindrical part is 10 mm. in the case of stills holding less than 20 tons, and 13 mm. for stills holding from 20 to 40 tons; the plates for the top and the bottom have a thickness of 15 to 18 mm.

At one of the largest English tar-works they employ stills of the shape sketched in Fig. 84, which have been working there for a number of years and give the fullest satisfaction. It will be noticed that the rise of the bottom is very much greater than in the stills already figured, so that, in fact, the crown of the bottom dome is quite half-way up the cylindrical portion of the still. This causes the heat of the fire to penetrate well into the interior of the mass of tar or pitch, and keeps the level of the pitch at the end of the distillation at a convenient height above the flue. These stills hold 14 tons of tar and require sixteen hours before running off the pitch, so that they can be

newly charged every day. In lieu of a running-off cock or valve there is a pipe (*a*) reaching down to the lowest part of the still, and continued outside in a cock (*b*) and a branch (*c*), descending into a closed tank (*d*). At the end of the distillation, and after the pitch has been softened, as may be required, by pumping tar-oils back into the still, a vacuum is produced in *d*, and after opening the cock *b* the pitch will rise through *a* and *c* and flow into *d*.



FIG. 84.

These stills require only 1 ton of coal or  $\frac{1}{2}$  a ton of creosote oil for distilling the whole charge (14 tons) of tar.

Similar stills are used at another of the very largest English tar-works; they hold 10 tons. Recently some stills have there been made to hold 20 tons, keeping to the same horizontal section and curve of top and bottom, and merely making the cylindrical portion so much higher; there seems to be a saving of fuel in the latter case. The 10-ton stills require twelve hours for distilling, three hours for cooling down till the pitch can be run off, and another four hours for filling. The firing is here (as

in some other works) exclusively done by means of creosote oil, of which only 50 to 60 gall. are consumed in working off a 10-ton still, which must be considered a very good result.

Many works employ a very different shape of still, viz., *horizontal cylinders* similar to steam-boilers. They are of course less in diameter (rarely above 7 ft.), but longer, than upright stills. It would seem that they require more fuel than the latter form of stills, and that the tar has much more tendency to froth over in them during the first period of the distillation.

At a German works I found such horizontal stills, holding 18 tons and provided with two or three still-heads, which were pronounced to work very satisfactorily. At another factory I saw horizontal stills, holding 22 tons, which required forty-eight hours for distilling off a charge, apart from the time for filling and cooling down, so that only two charges could be made per week. The plates have a thickness of 12 mm. at the bottom, and 14 mm. at the top (that is, slightly below and slightly above  $\frac{1}{2}$  in.). They are made thicker at the top, because they suffer more where they are not in contact with tar or pitch, and are more reduced in thickness by working than the bottom plates—an observation which I have found confirmed in the case of English upright stills. The setting of the horizontal stills is best made in such a way that the flame does not directly touch the bottom of the still for about two-thirds of its length, but is kept off by an arch perforated with pigeon-holes; the last third of the bottom is heated by the direct flame, the bottom of the flue being 12 in. below the lowest part of the still.

In America the most usual shape of tar-stills is also that of horizontal cylinders, made of  $\frac{5}{8}$  in. steel plates of about 2000 gall. capacity or more. There is only one row of rivets along the top.

Special forms of tar-stills have been described by the following inventors:—

Uhlig (*J. Soc. Chem. Ind.*, 1910, p. 195) describes a still, specially intended for water-gas tar, consisting of a slanting cylinder which is heated, beginning from the upper end and going down to the lower end; this causes the distillation to go on regularly and without bumping.

Kusch, Teubner, and Deutsche Erdölwerke describe in their Ger. P. 220657 a horizontal still, containing inside below the top a curved division-plate, leaving a slit along the sides, so that the vapours pass through it and go away at the top, whilst the oily particles carried away fall back into the still.

In my and Dr Köhler's opinion, horizontal stills are altogether inferior to upright ones; they work much more slowly, and they consume incomparably more fuel than the latter. At a works where horizontal stills are used, the manager told me that 1 ton of coal, or an equivalent of other fuel, would distil 5 tons of tar; whilst at several other works, where upright stills are used, I found that only *one-third* of that

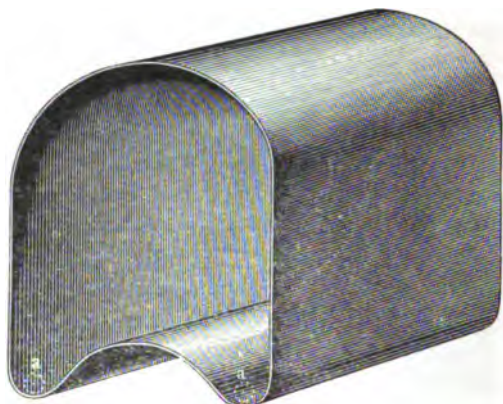


FIG. 85.

amount of fuel was consumed. This is confirmed by Warner (*J. Gas Lighting*, 1910, p. 132). In a factory where horizontal stills are working, they burned  $3\frac{1}{2}$  cwt. coal to each ton of tar; whilst at other factories, working with upright stills, only  $1\frac{1}{2}$  cwt. per ton of tar was consumed. The case may be different at factories where the waste heat of the stills is employed for other purposes, or where the stills are provided with stirring-arrangements.

Stills of a very peculiar shape are employed at the Paris gas-works. They are *wagon-shaped*, with an incurved bottom, and edges very much rounded (Fig. 85), holding only 1440 gall. of tar. The flues run twice round the sides of the stills. This shape, I am informed, is preferred because it causes the

least injury to the metal in contracting and expanding with the changes of temperature. But such injury has not been observed where the usual upright cylindrical stills are at work; and the Paris shape has from the first the disadvantage of requiring two running-off taps, one for each side (at *a a*). These stills are set so that the bottom is not touched at all by the fire, which circulates twice round the sides. In the lower flue the flame does not impinge directly upon the metal, which is protected by thin firebricks; in the upper flues these are not employed. Everywhere else I have found the flame (which has expended its greatest heat upon the curtain-arch beneath the still-bottom) heating the sides of the still without any firebrick lining and without doing any injury to the still. The stills at those works do not show the arrangements mentioned by Girard and Delaire<sup>1</sup> and by Wurtz,<sup>2</sup> by which, as soon as the level of the tar sinks too low, the upper flue is shut off and the flame is only allowed to circulate in the lower flue. But anyhow the flues heat only the lower part of the still; so that such a complicated arrangement is not called for. Even the upper flue is built in such a way that the level of the pitch at the end of the distillation is still above it—which is not very difficult to manage, since the bulk of the pitch is at least half of that of the tar.

Kissel (*Z. angew. Chem.*, 1893, p. 61) prefers this shape to all others. The stills working at his factory were made of the best quality of wrought-iron, the bottom of charcoal-iron. Their dimensions were: length 5 metres, width 2 metres, height from the lowest to the highest point 2.70 metres; taking a charge of 20 to 30 tons of tar.

Another shape of wagon-still is shown in Figs. 86 and 87, according to Engler (*Dingl. polyt. J.*, 1886, vol. cclx., p. 435), as employed in the Baku petroleum-refineries. They are up to 23 ft. long, 13 ft. wide, and 10 ft. high. *a a* are the still-heads; *b* a manhole; *c c* three outlets for the residues. The arrangement of the internal stays is clear from the diagrams. There are two fireplaces (*r*) supplied with "astatki" (pp. 329 *et seq.*; I have seen tar-stills worked with creosote oil, when this was unsaleable!); the flame first passes through the arched-over flues B, B<sub>1</sub>, returns at the still-end to the fore part, rises up,

<sup>1</sup> *Dérivés de la Houille*, p. 8.

<sup>2</sup> *Matières colorantes*, p. 23.

travels again backward along the sides of the still, then downward and through the flue  $B_2$  into the chimney.

J. Maxwell (B. P. 3640, 1882) places vertical pipes within

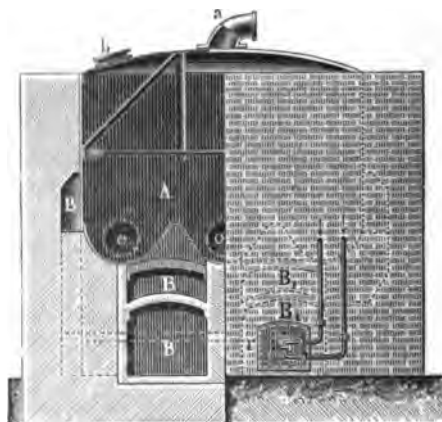


FIG. 86.

the stills, with or without the use of a compressed-air tube, for the purpose of facilitating the separation of water, oil, and other liquids from the tar while undergoing distillation.

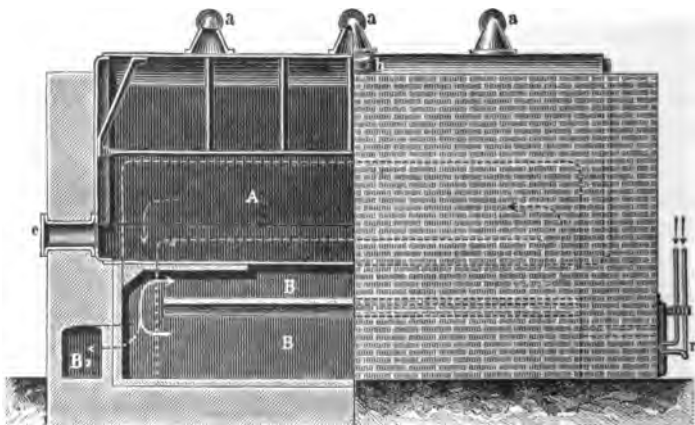


FIG. 87.

*Stills with mechanical agitators* will be described on pp. 459 *et seq.*

During recent years endeavours have been made to economise fuel for the tar-stills by means of *inward heating*

*arrangements.* As Rispler (*Chem. Zeit.*, 1910, No. 31) has shown, the utilization of the fuel in the ordinary stills is very imperfect. In his experiments with an upright still, filled with water, 1 part by weight of coal evaporated no more than  $2\frac{1}{2}$

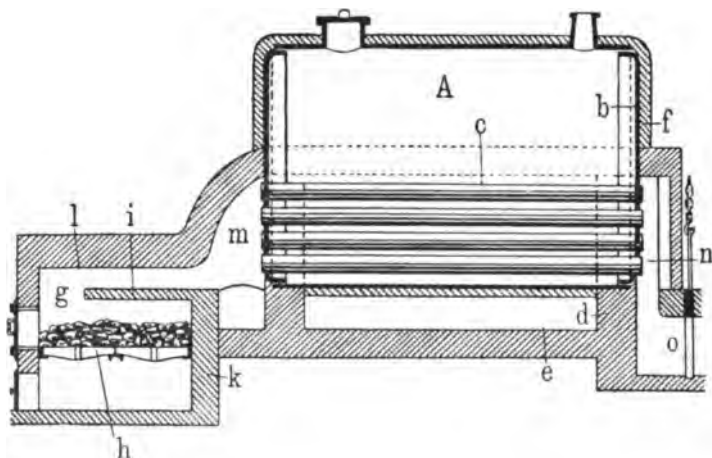


FIG. 88.

parts of water, which, of course, is a very imperfect result, which can be considerably improved by heating the stills, also by heating-tubes inside.

One of the best apparatus for this purpose is shown in the German patent, No. 153322, of the Chemische Fabrik Lindenhof, C. Weyl & Co., at Mannheim, illustrated by Figs. 88 and 89.

The still is a horizontal cylinder of any desired capacity through which pass numerous heating-tubes, the top layer of which always remains below the level of the liquid, up to the point where only pitch remains behind, so that there is never any risk of overheating the charge. The fireplace is arranged

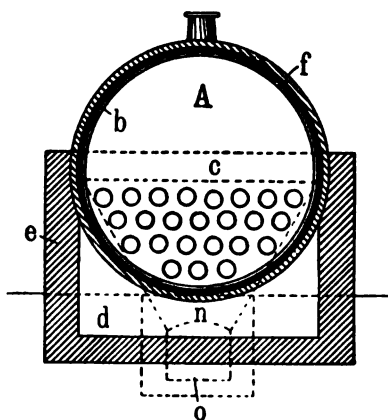


FIG. 89.



in front, so that only the hot fire-gases pass through the tubes. The still is supported by brick pillars at both ends, the other part of the still-bottom being free, protected against cooling by good insulation. This not merely saves a good deal of the cost of brickwork, but also leaves the cylinder mantle free for any repairs. The only brickwork required is that of the fire-place, and that of the flue leading to the chimney. This still allows of thoroughly utilizing the heat of the fire-gases, and moreover divides the heat upon its contents of tar in such a regular way that crude tar, without previous dehydration, can be distilled down to pitch; there is no over-heating, nor any violent bumping during the boiling. It can be worked with a vacuum, with all the advantages in respect of saving of fuel, time, and attendance connected with it. It has proved to be an excellent apparatus in actual work.

Other stills of this description are shown in the German patent, No. 150229, of Louis Schwarz & Co., at Dortmund, and in the German patent of Barlen, No. 228297, by Borrmann (*Z. angew. Chem.*, 1915, i., p. 387; Crossley, Wheeler, and Smith, B. Ps. 707 and 19392, of 1914), who superheat the froth.

*Detailed description of a Tar-still and the auxiliary apparatus belonging to it.*

*The various parts belonging to a tar-still* are best described along with an explanation of Figs. 90 to 92. These represent a 25-ton still, the details of which, as well as those of the setting, are not copied from a particular plant existing at a factory, but combine those features of all the apparatus observed by myself in England and Germany which seem to me most practical. But each single part, described or drawn here or hereafter, is actually in use at one or another of the largest and best works.

Fig. 90 is a cross-section along the line E F of the plans; Fig. 91, a plan laid through C D of Fig. 90; Fig. 92, a plan of the still itself, along the line A B of Fig. 90,—all  $\frac{1}{8}$  of the natural size. The still is 9 ft. 10 in. wide, and 11 ft. 6 in. high (without the dome), made of  $\frac{3}{8}$ -in. or  $\frac{1}{2}$ -in. boiler-plate. The inward curve of the bottom is about the same as the outward curve of the top; both of them are sometimes made much higher than shown here. The still may be set with a slight slope towards the outlet-cock *a*, which in any case is placed as nearly as

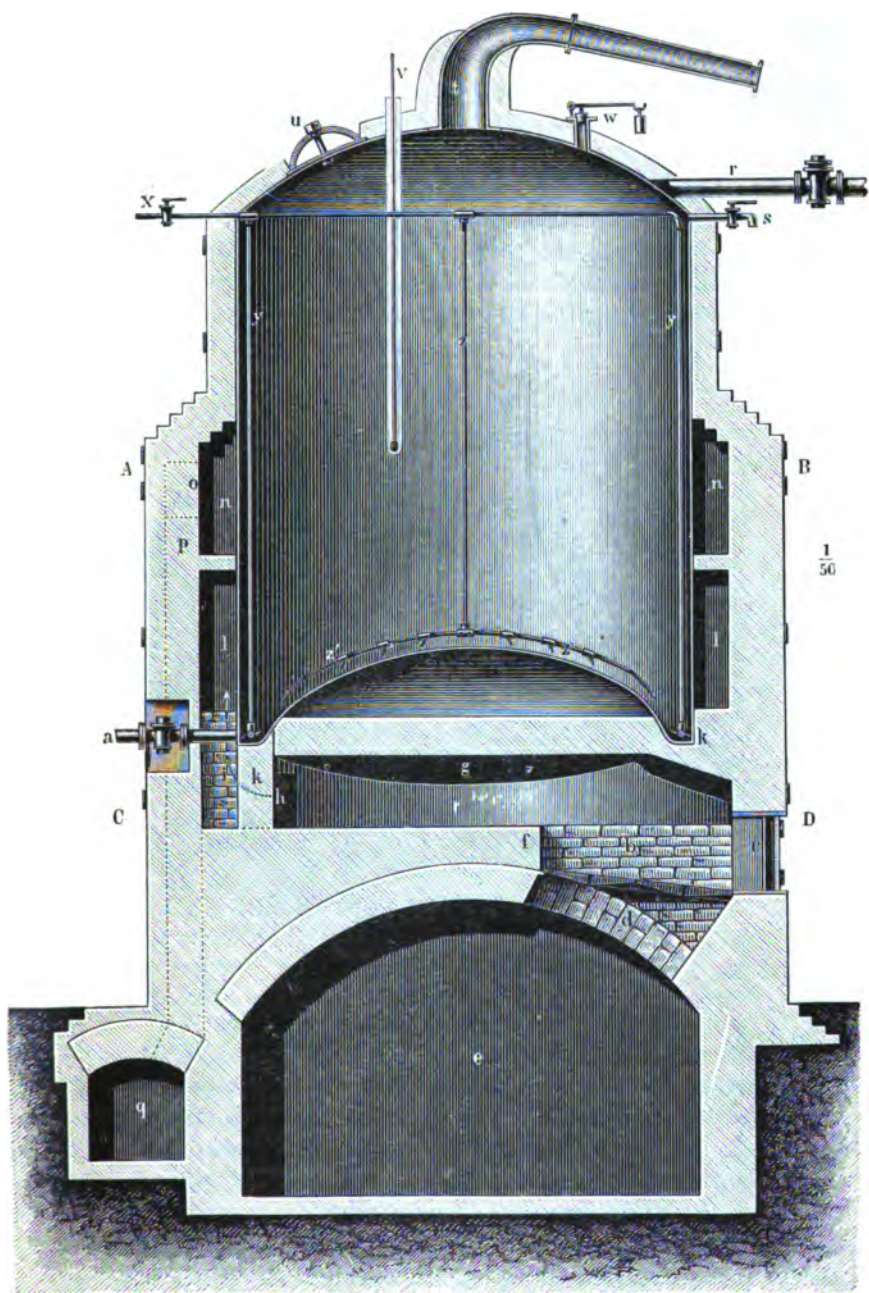


FIG. 90.



our diagrams we show the arrangement at one of the largest English works. Here the ash-pits are closed below the fire-doors, and all of them communicate by an opening (*d*) with a large overarched passage (*e*) running along the whole set of stills and only accessible from the two extremities; this affords perfect security against fire in case of the tar boiling over and running out of the receivers. It is true that other precautions can be taken against this danger, such as constructing the

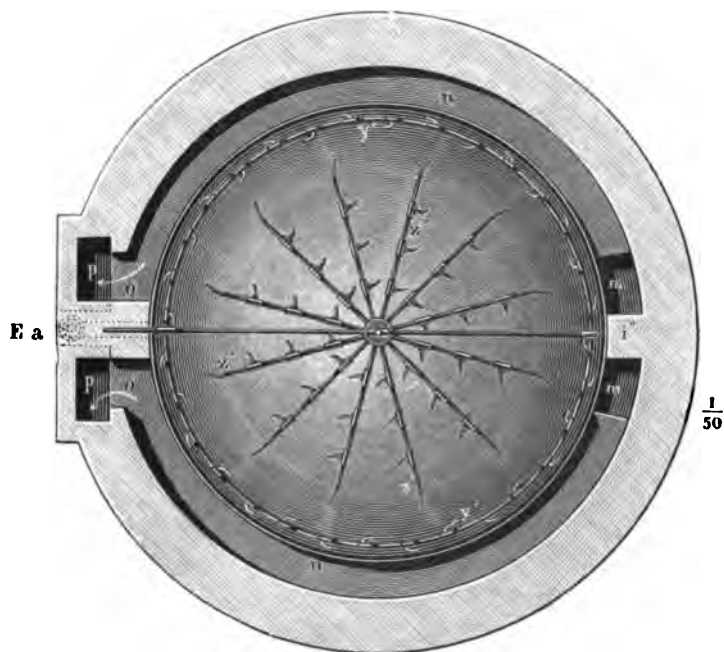


FIG. 92.

receivers in the manner to be described below, where the tar, even if it boils over, cannot get at the still-fires; but the arrangement shown here will also act in the case of accidents to the pipes and, especially, to the still-head, for with it the vapours issuing in great force cannot take fire at the ash-pits. Moreover, the underground passage *e* permits great cleanliness. It is useful to place a steam-pipe below each fire-grate, to increase the draught, to prevent overheating of the grate-bars and the fire-bars, and thus to avoid the formation of fluxed cinders.

Such a steam-pipe also allows of extinguishing a fire, caused

by tar leaking out of the still. Steam is not merely more efficient for this purpose than water, but it also avoids the danger of an explosion which might take place when liquid water meets burning tar or pitch, in consequence of the sudden evaporation of the water.

The flame travels over the fire-bridge *f*, and under the arch *g*. This arch is sprung barrel-shaped from the annular wall *k k* on which the still is seated, and completely shuts off the still-bottom from the flame. Thus the space between *g* and the still-bottom is an air-bath, kept very hot by the flame below *g*, but never excessively so. So much heat is imparted to the arch *g* that at the end of the operation no firing is needed, especially if steam or exhaustion be applied. The weight of the still resting upon the annular wall *k k* enables this all the better to support the pressure of the curtain-arch *g*, which is otherwise independent of the brickwork of the fireplace, and can be easily renewed when it is too much burnt out. The flame now travels on through four holes (*h h*) into two vertical flues (*i i*), and arrives at the cylindrical shell of the still. The solid pillar *i'*, between the flues *i i*, is continued to the top. Through this pillar passes the pipe connecting the pitch-cock *a* with the still, protected from the fire, but kept warm by the flues *i i* and *p p*. This pipe should be at least 12 in. wide, to prevent choking-up. The pillar *i'* forces the flame to divide into two currents, which pass round the lower part of the still in the annular flue *l l*; they are prevented from uniting in front by the pillar *i'*, pass through the flues *m m* into the upper annular flues *n n*, return to the back part, and enter through *o o* into the downcast-shafts *p p*, communicating with the main flue *q*. The shafts *p p* are provided in suitable places with dampers, by which equal heating of both sides of the still can be secured. For shallower stills a single annular flue would be sufficient; its downcast-shafts would have to be arranged in front, at each side of the fireplace. The best width of the annular flue is from 9 to 12 in.

The outer wall, as far as the flues reach, should be at least 14 in. thick, and should be strengthened by several iron bands, shown in Fig. 90. Above the flues the still is surrounded by a 9-in. brick jacket to prevent cooling; the brickwork continues along the whole top, and preferably also up to the top of the still-head *t*. Such a protection against cooling is all the more

needed where the tar-stills are exposed to the air, or merely covered by a light corrugated iron roof, etc. This, the most usual, style causes any explosions or fires to be less destructive than if the stills were placed in a substantial building. It is advisable in that case to protect the brickwork of the stills against rain by a coat of molten pitch.

*The mountings of the still* are as follows :—A cast-iron *supply-pipe* (*r*, Fig. 90), closed by a slide-valve or cock, is provided for running-in the tar. It is best rather wide, say 6 in., so that not much time may be consumed in filling the still. Where the tar is not pumped, but run in from a high store tank, a simple hole will do, afterwards closed by a screw-plug, or even the manhole. There may be a special hole, through which the depth of the tar can be gauged ; but an *overflow-cock* (*s*) of 1-in. bore is preferable. As soon as tar comes out of it the feeding is stopped and *s* is closed. We have seen on p. 389 that, during the heating up, the water collecting on the top of the tar can be removed from time to time by opening *s*, which greatly assists the work. If the tar is pumped by compressed air, in which case the pressure-vessel serves for measuring its quantity, the gauge-hole and overflow-cock are unnecessary, since the filling-pipe serves at the same time as overflow.

The tap (*a*, Fig. 90) serves for *running off the pitch* ; it will be described more exactly hereafter. Instead of connecting it, as is here shown, by a 4-in. pipe with the still, the latter is better provided with a 12-in. pipe projecting through the brickwork, and in this the tap *a* is fixed. If the setting is similar to that shown here, the pipe is always hot enough, for the pitch to remain liquid. But it is possible to work altogether without a tap, by forcing up the pitch through a vertical delivery-pipe by means of steam (*cf.* below).

The vapours are carried away by the cast-iron *still-head*, *t*, which usually decreases in width from 12 in. down to 6 in., and is then continued into a 6-in. metal-pipe, leading to the condensing-tank. Sometimes a gutter is provided inside the still-head, at its base, to conduct directly outwards any liquid condensing in the rising part of the head, so that it cannot drop back into the still, where it might cause frothing-up ; but this is hardly necessary if that part of the still-head is surrounded by a bad conductor of heat. In some places they put a steam-

pipe into the still-head, in order to remove obstructions by blowing through it. But a still-head of such a width cannot very well become obstructed if it has a little fall. As to the connection of the still-head with the still-top, we have described it on pp. 400 and 403.

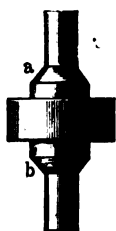
In the connection between the pipe connecting the still-head with the condensing-worm it is necessary to consider the expansion of the iron by higher temperatures. The connecting-pipe is usually made of wrought-iron.

Every tar-still must have a *manhole*. We have represented this at *u* (Fig. 90), like a steam-boiler manhole, closed by a cover fixed on by an arm and screw-bolt; the joint is made by a ring of asbestos packing. In Fig. 84 it is shown how the manhole is combined with the still-head, which saves cutting a special opening in the still-dome. The lower side of the manhole lid is best made to slope towards a centre, where an open spout leads to the top of the condensing-worm. The object of this is: to prevent the water condensing there in a liquid form from dropping into the contents of the still and causing these to froth over. Anyhow, this water, condensing both there and on other fittings, should not be allowed to run down the sides of the still, where it might cause a corrosion; this is done by allowing these parts to continue an inch or so into the inside of the stills. In some places the manhole lid is made to serve at the same time as a *safety-valve*. It is then a plate, loosely laid upon a riveted neck, and joined to it merely by some cement which does not become too hard. If the pressure within the still should for some reason or another mount too high, the lid will be thrown off before any other damage can occur.<sup>1</sup> In America some tar-stills are provided with a steel pin loosely fitting into a hole in the still-cover; when there is pressure in the still, the pin is ejected and vapours issue from the hole, which is a signal for opening the fire-doors and blowing steam through the worm. Unless some such contrivance is provided, there should be a proper safety-valve present, as delineated here at *w*; but many

<sup>1</sup> Watson Smith (*J. Soc. Chem. Ind.*, 1882, p. 342) doubts whether this contrivance would be efficient—either it would be too tight, and thus not act at all, or else it would be too loose, and thus allow vapours to escape at the end of the process. But I am acquainted with a very large and excellently managed factory where the above-described arrangement has worked perfectly for a long time.

tar-stills are found without one. A very useful precaution consists in providing a side branch to the safety valve, which permits any tar that boils over to run to some safe place away from the still, preferably back into the tar-pit.

Hamilton (*Chem. Trade J.*, xxi., p. 87) shows a cast-iron valve, Fig. 93, where *a* and *b* are ground together; the weight (not shown here) rest on *a*. Fig. 94 represents a cast-iron valve used in Germany. A is a case with removable cover and two 6-in. branch-pipes. On the turned bottom fits the turned plate



B with guide C, passing through the stuffing-box D. The valve is fixed to the still at E; at F is fixed a pipe leading to a somewhat distant reservoir. The joint between A and B is made with asbestos packing. In case of

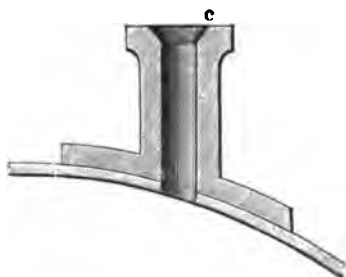


FIG. 93.

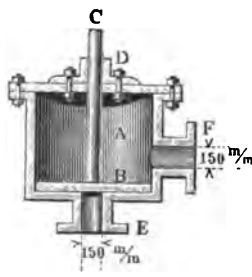


FIG. 94.

pressure within, the plate B rises up and the vapour escapes through F. Near the rod C there may be an electric contact for indicating its rising.

Hoffmann's safety-valve for tar stills, petroleum tanks, etc., sold by the Chemische Fabrik Salzkotten, is described in *Chem. Ind.*, 1905, p. 434. This valve automatically opens when a certain pressure exists within the apparatus, and below it within the still; a thin-meshed metallic tile prevents the striking-in of a flame which may be formed by the escaping gases.

If a *thermometer* (*v*, Fig. 90) is used, it should be placed in an iron tube closed at the bottom and filled with iron filings or mercury; it should reach half-way down the still. In lieu of this, some works have pyrometers of various constructions,



mostly not very reliable in their indications. Unless steam be applied in the last stage of the process, a mercurial thermometer cannot be used, since mercury boils at  $360^{\circ}$ ; in that case it must first be taken out of the iron tube. It should not be forgotten that mercurial thermometers which have been exposed to a high temperature for some time vary their fixed points considerably, owing to deformations of their bulbs; such variations have been observed extending to as much as  $14^{\circ}$ . Hence they must be compared with a standard thermometer from time to time; otherwise mistakes in the working and disputes with buyers may occur. This of course holds good of all thermometers used at tar-distilleries.

In German works the distillation is rarely carried on by the indications of the thermometer: the work is done by means of practical indications, to be mentioned below, and by the specific gravity and behaviour of the distillates.

The following precautions should be observed *in fixing pipes and mountings to the stills*. The iron is mostly corroded in those places which are not in contact with tar—that is, at and near the top; this shows that not the tar itself corrodes the iron, but the vapours, and still more condensed ammonia-water, more particularly by the ammonium sulphide. Köhler (*Z. angew. Chem.*, 1894, p. 513) found the worst corrosion where, in consequence of joints leading outwards, the plate was cooled, *e.g.* at the manhole and at pipes flanged on to the still, where the thickness of the iron had diminished from  $\frac{1}{2}$  in. to  $\frac{1}{8}$  in. This was done away with by carrying the pipes 6 in. into the still, and protecting them against cooling on the outside.

Care should also be taken that the thermometers, valves, manholes, etc., are inserted absolutely tightly. If this is not the case, benzene vapours will issue in the first part of the process, and as these form an explosive mixture with air (in the proportion of 1 benzene to 35 air), bad accidents might occur.

The reader will notice in our diagrams (Figs. 90 and 92, pp. 411 *et seq.*) a system of *steam-pipes* (*xy s*). We shall see afterwards that the majority of works now employ steam, mostly superheated, for finishing the process. This is usually done by means of a cross-shaped tube with perforations for the issue of the steam. Here we have shown the more perfect arrangement patented by Trewby and Fenner (No. 3613, 9th Sept. 1879).

The steam is introduced by a 1-in. pipe with tap ( $x$ ), which sends down three vertical branches ( $y \ z \ y$ ) inside the still. The tubes  $y \ y$  communicate with an annular-shaped tube,  $y'$ , placed in the lowest part of the still, and  $z$  with a system of branch-pipes,  $z' \ z'$ , covering the whole still-bottom. Both  $y'$  and  $z \ z'$  are provided with a large number of open, slightly bent outlet pipes with contracted ends. Thus the steam is divided into many thin jets, ranging all over the bottom of the still, which prevent its overheating and carry away the vapours of the heavy hydrocarbons. Owing to the large surface of the steam-tubes, the steam is superheated before issuing, and a special superheater is unnecessary.

Later on, H. W. Fenner (B. P. 13629, of 1884) combined the application of stirrers with that of steam, by providing a hollow shaft, passing down the centre of the still, with branch-pipes for distributing the steam, the whole system being made to rotate by suitable gearing.

#### *Setting the Tar-stills.*

One of the usual ways of setting tar-stills in England is shown in Fig. 95.<sup>1</sup> Here there is no curtain-arch at all; the fire of the grate  $a$  passes through the holes  $b$  in the annular wall  $c$ , and once round the still in the flue  $d$ . Sometimes the annular wall supporting the still is strengthened by iron bearers, which probably do not last very long.

From a communication kindly made to me in 1885 by Mr John Wyld, of the Bradford Corporation Works at Frizinghall, it appears that at one or more works in that neighbourhood the system of firing by gas-producers was applied to tar-stills, but it is not stated whether it was found to possess any advantage. There is no reason why it should not answer, as the firing could be more easily regulated; but I should not expect to find any saving of fuel by that method.

H. W. Fenner (B. P. 13630, of 1884) forces the flame to touch the bottom and sides of the still in a particular manner.

The plant described by Toldt (*Chem. Zeit.*, 1898, p. 258) does not show any special features.

<sup>1</sup> From *Chemistry Applied to the Arts and Manufactures*, by Wm. Mackenzie, vol. i., p. 499. The other figures found in the same place, taken from Bolley's *Technologie der Gespinnsfasern* (pp. 210 *et seq.*), do not refer to the distillation of coal-tar, but to lignite-tar.

Louis Schwarz & Co. (Ger. P. 150229) describe a new way of setting tar-stills, which is to avoid the drawbacks connected both with the solid arch below the still-bottom, as shown in Fig. 90, p. 411, and with the unprotected bottoms, as shown, *e.g.*, in Fig. 95. The former arrangement involves a considerable loss of heating-power, the latter leads to the forma-

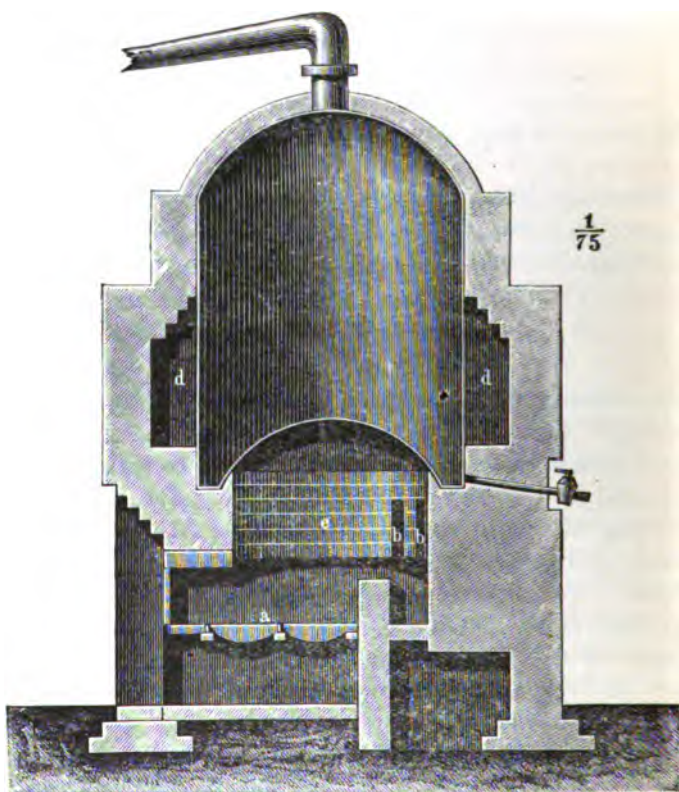


FIG. 95.

tion of coke. The new invention starts from the fact that a coating of coke is much more easily formed on the bottom than on the perpendicular side-walls of the still. It retains the protecting arch, but between this and the still-bottom a hollow space is left, which is connected on one side with the annular flue round the sides of the still by a tube, passing through the still itself, on the other side with the exit-flue by means of a down

corner. The heating-gases thus first pass through the annular flue round the still, and then underneath the bottom, without subjecting this to serious overheating, while the tube passing through the retort still further increases the heating-surface.

*Condensing-Apparatus.*

Girard and Delaire (*Dérivés de la Houille*, pp. 8 and 10) state that sometimes a still is provided with three condensing-

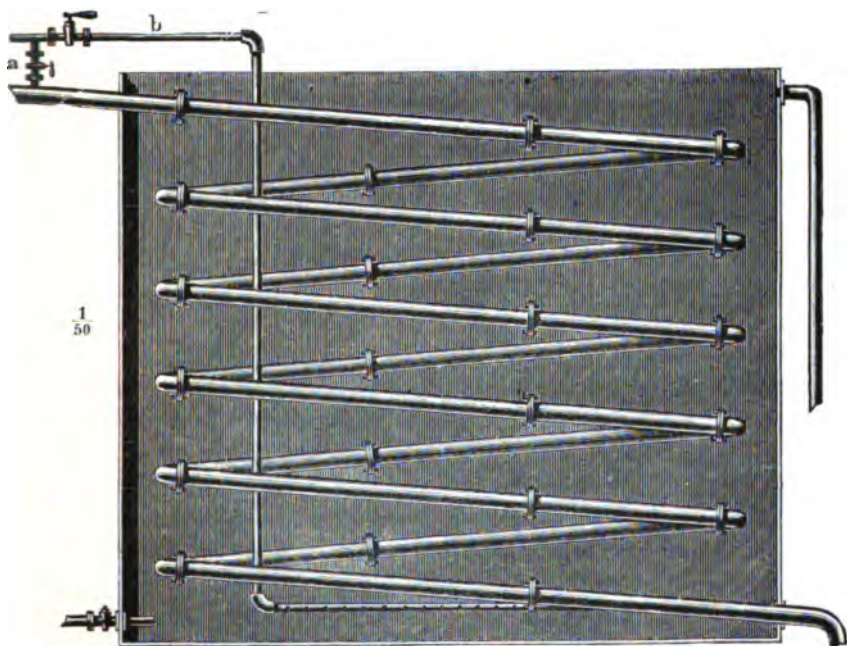


FIG. 96.

worms, each regulated by a stopcock, and consecutively employed for the different fractions. None of the works known to me use that kind of apparatus, the object of which is not very clear, since the separation of the fractions need not commence in the worms, but can take place in the receivers. I have never observed more than one condensing-worm; but very different kinds are used. The English works mostly employ cast-iron pipes, in lengths of 9 and 6 ft., from 4 to 6 in. wide, and connected by elbow-pieces (Figs. 96 and 97).

The whole is contained in a wrought-iron tank and is supported by strong iron stays (not shown in the diagrams). The tank being rather narrow, two worms, belonging to different stills, are occasionally placed in it. Formerly the elbows were sometimes provided with cleaning-out holes; but these are quite unnecessary, if the pipes have sufficient fall and if the tank at

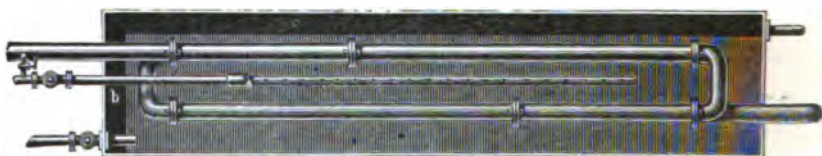


FIG. 97.

the end of the process is kept warm. But it is always advisable to put a steam-pipe (*a*) in the top pipe, so that the worm can be purified by blowing steam through it in case of need. Anyhow there should be a steam-pipe (*b*) for heating the water surrounding the worm.

At some English works the horizontal section of the cooling-

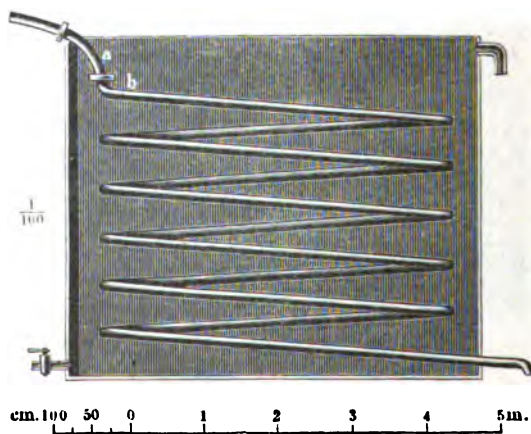


FIG. 98.

system is not, as here shown, oblong, but square; this entails the use of very large water-cisterns to contain the worm.

*Metal for the Cooling-worms.*—Sometimes these worms are made of lead. In this case the cast-iron pipe *a* coming from the still (Fig. 98) must be continued at least a foot below the level of the cooling-water, and the lead pipe *b* must

commence there; otherwise the latter might easily be melted at the end of the process by the heat of the vapours in the part not cooled by water. We cannot, however, recommend lead for the cooling-worms of tar-stills. Apart from its low fusing-point, the worms made of it have much less cooling-power than iron worms, and frequently cause repairs by settling down. They are nowadays only found at very small tar-distilling works.

Spilker (*Kokerei und Teerprodukte*, p. 43) recommends the employment of cast-iron for the cooling-worms, as well as for the still-head and the connecting-pipes, because it is much less acted upon by the ammonia present in the vapours than wrought-iron. Rispler (*loc. cit.*) points out that wrought-iron worms are, however, not merely cheaper than cast-iron worms, but, owing to their thinner walls, have a much better heat-exchanging power than those made of cast-iron. They can be employed without hesitation for condensing all the vapours formed below  $280^{\circ}$ . Their corrosion only takes place at higher temperatures (at the end of the distillation  $360^{\circ}$  may be attained) in consequence of the dissociation of ammonium chloride into free  $\text{NH}_3$  and  $\text{HCl}$ . This causes a corrosion of the top coil, but lower down  $\text{NH}_3$  and  $\text{HCl}$  again combine to  $\text{NH}_4\text{Cl}$  which does not act upon the metal. Cast-iron cooling-worms are much less acted upon, and may go on for years without repairs, but the cast-iron must be of the best quality, and not porous. Since cast-iron worms always have unsound places, it is best to employ straight pipes, cast in the vertical position, and connected by short curved pieces.

Warnes and Davey (*J. Soc. Chem. Ind.*, 1910, xxix., part 1) also believe that the corrosion of the iron is principally caused by the ammonium chloride, but also by the sulphide, sulphocyanide, and cyanide of ammonium.

Engler (*Dingl. polyt. J.*, ccix.) describes the following system of cast-iron refrigerators, frequently used at the Baku petroleum-refineries (Figs. 99 and 100). There are always four pipes in a horizontal plane, joined by a cross-pipe ( $b$ ,  $b_1$ ,  $b_2$ ), etc., and six such systems one above another, altogether 24 pipes, with a total length of 200 to 300 ft.; the top pipes have a width of 8 in., the middle ones 8 in., and the bottom pipes  $5\frac{1}{2}$  in. The vapours enter through  $a$ , spread on the cross-piece  $b$ , pass

across through four pipes to the second cross-piece  $b_1$ , then downward to  $b_2$ , back again through four pipes to  $b_3$ , and so on down to the outlet at  $b_{11}$ .

The majority of German works prefer drawn wrought-iron tubes of at least 2 in., better 4 to 6 in., bore, bent in the

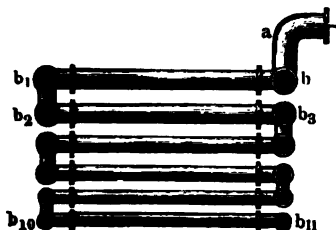


FIG. 99.

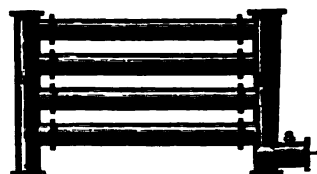


FIG. 100.

shape of three-quarters of a circle (Fig. 101) and connected by screwed-on flanges. With these there are no uneven places at the joints and no sharp angles as with the cast-iron worms. Even better than these tubes are wrought-iron worms each made in a single piece, as supplied by some Rhenish ironworks.

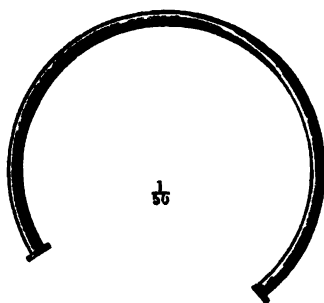


FIG. 101.

These worms are always contained in circular iron tanks provided with a steam-pipe. Wrought-iron or lead worms cool better than those made of cast-iron, owing to the smaller thickness of metal. Their narrowness is a drawback, which is, however, of not much consequence where the distillation is carried on by the help of a vacuum. The thorough cooling taking place in such narrow wrought-iron tubes is all the better for keeping up the vacuum.

In Germany the refrigerators are about 7 ft. wide and from

7 to 10 ft. deep, with narrowly coiled worms, making the length of pipe from 200 to 300 ft., according to the size of the stills.

In England, according to Warnes (*J. Gas Lighting*, 1910, p. 132), the diameter of the cooling-pipes varies from 2 to 4 in.; their total length from 130 to 300 ft. For a 20-ton tar-still the length of the worm-tube should be about 130 ft., its width 3 in.

According to J. Brönnner, in lieu of cooling-pipes, a double cylinder can be employed, water being run through the ring-shaped space round the inner cylinder. This avoids all danger of stopping-up.

As *cement* for the joints the ordinary rust-cement (made of iron borings, sulphur, and sal-ammoniac) can be employed. In lieu of this another cement may be used, which is as tight, but is more easily removed. It is made by slaking lime to a powder, which is sifted and then kneaded with a little water to a stiff dough-like putty. This lime-putty is stemmed into the joints, hardens in twenty-four hours, and is perfectly tight against water and oils, either liquid or in the state of vapour; nor does heat affect it; only it must not be exposed to direct fire. For joining flanges, asbestos packing is no doubt the best possible material.

Instead of a condensing-worm, some works employ a double cylinder with a current of water in the annular space between the cylinders. Such a contrivance is evidently not exposed to being stopped-up.

The condensing-pipe is slightly bent upward where it leaves the tank (Fig. 104 at *a*); and at this place an upright pipe (*b*) is fixed, through which the permanent gases escape, whilst the liquid products run into the receivers. We shall see later on that the escaping gases ought not to pass directly into the atmosphere, but first through some purifying-apparatus.

Sometimes the bottom end of the condensing-pipe is fitted with a two-way or three-way cock, for changing the receivers and for conducting the contents of the still, in case of its boiling over, back into the tar vat. These aims are, however, better attained by means of the separating-box, shown below. We cannot recommend using a tap in this place (at the end of the cooling worm), as it is too easily plugged up by solidifying naphthalene, etc.

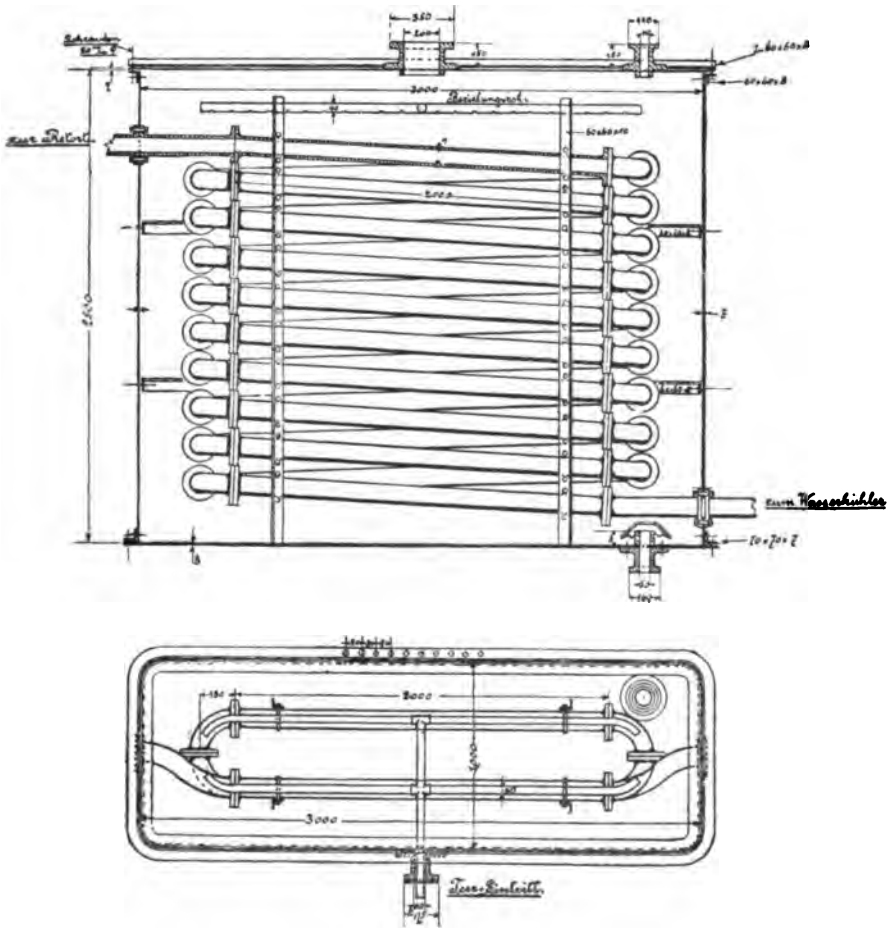


Ellison and Davis (B. P. 13929, of 1886) employ the condensing-heat of the vapours for heating-up another charge of tar. In lieu of an open cooling-tank they employ a still placed at a higher level with a worm into which the vapours from the tar-still are introduced at the top, whilst its bottom is connected with an ordinary cooler. When the distillation is finished and the pitch run off, the heated tar from the upper still is run into the lower tar-still and is distilled there as usual. The vapours escaping from the top still are of course condensed.

A similar plan has been patented by Max Böhm & Co. (Ger. P. 60747). We shall meet with the same principle in various patents to be mentioned later on. Gröling and Estlander (Ger. P. 98928) describe a special kind of heating-up apparatus, serving as dephlegmator for the gases from the still. Rispler (*loc. cit.*) states that in a factory working with stills of a capacity of 32 tons a pre-heater was employed, filled with tar, and containing the cooling-worms of two stills, whereby the charge of a still (= 32 tons) was heated up, and the water and light oil distilled off, so that the tar coming out of the pre-heater was free from water and light oil, and required only 5 per cent. coal for distilling it down to pitch, against  $7\frac{1}{2}$  per cent. required for raw tar. Part of this saving of fuel is certainly compensated by the greater cost of plant for this system, and several other drawbacks also occurred. Rispler therefore constructed a preheater, which has done satisfactory work on the large scale. Fig. 102 shows it in vertical section, and Fig. 103 seen from above. Above the worm there is a perforated pipe of the same shape. In the cover of the pre-heater there are fixed two short pipes, one for the alembic conducting the vapours to a cooler, the other for a safety-valve with lateral blowing-off pipe. All the blowing-off pipes of the factory are connected with a common pipe, leading to a vessel placed in the open air. At the bottom of the pre-heater there is a pipe-neck, ending about an inch above the bottom, covered with an iron bell-jar and connected by a pipe with the reservoir for pre-heated tar. The bell-jar prevents the vapours formed in the pre-heater from escaping with the warm tar. During the working of the pre-heater, the vapours coming from the tar-stills travel through

the worm which is covered by tar flowing out of the perforations of the pipe above, thus effecting a good exchange of heat and a quick evaporation. The heated and partly distilled tar at

FIG. 102.



**FIG. 103.**

once runs away at the bottom, so that no considerable pressure can occur in the case of an accident, and there is no increased danger of fire. The distillate from the pre-heater is condensed in a special cooler.

*Receivers.*—In order to separate the different products, there must be a corresponding number of receivers, and the products running out of *a* (Fig. 90) must be run at discretion into any of these. Many contrivances may evidently serve for changing the receivers; but some points must be always observed. Thus the receivers for the first products should be tightly closed, to avoid both loss and danger of fire. Furthermore, the first receiver must be provided with some contrivance for easily separating the oily and watery portions. The receivers for carbolic oil and those for heavy oils should be easily accessible, in order to remove the crystalline masses always separating in them. Above all, it is imperative to take every possible precaution against fire. If the receivers are placed near the tar-stills, they must be separated from them by a solid wall. Any tar which might by accident boil over and run out of the receivers must under no circumstances be allowed to get near the still-fires or any other fireplaces. At some places the receivers are only just large enough to hold the product of one operation. This has the advantage that the manager can judge of the still-work by the depth of the liquor in the receivers; but then there must be another and larger set of store-tanks for every fraction. Hence the receivers are frequently at the outset so constructed as to contain a large quantity of products, in which case they are placed at some distance from the stills, and serve for a number of these at the same time.

Instead of dwelling upon the various ways in which receivers can be arranged, we prefer describing a special arrangement found at some of the largest works, and fulfilling the conditions of cleanliness, convenience, and safety. The distillates of every still run from the swan-neck pipe *a* (Fig. 104) into the glass jar *c*, in which the process can be well observed. A jar with hydrometer can be placed in it; samples may be taken from it; the rate of distillation is easily observed; the appearance of the products is noted, etc. When the oils become too hot, the glass jar can be replaced by an iron funnel. The glass jar *c* is closed by a sheet-iron cover, with a hole for the passage of the pipe *a*. This is fixed into an elbow pipe, *d*, which conveys the liquids into the tight *separating-box*, *e*. To this are attached as many taps (*f f*) as there are different fractions to collect. These are simple 2-in. gas-taps, made of cast-iron; brass can-

not be employed, on account of the ammoniacal liquor. The taps for creosote oil and anthracene oil may be larger, say 3-in. or 4-in. bore. The taps *f f* (in our diagram there are six) are connected by flanges with the pipes *g' g'*, which form vertical branches of the main pipes *h h*. The latter are laid in a

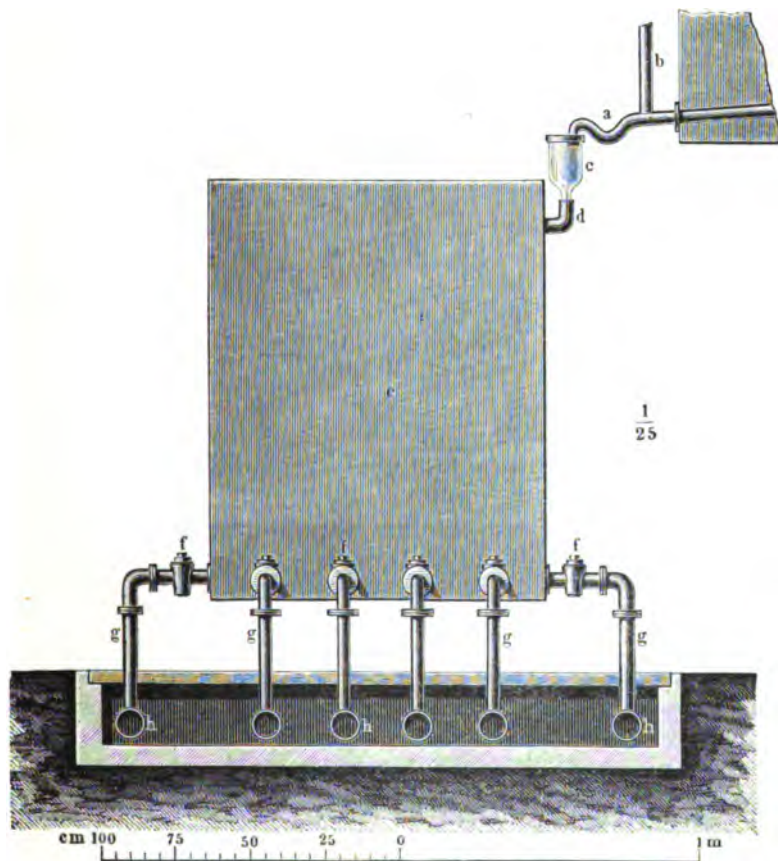


FIG. 104.

bricked pit running along the whole set of stills, so that the products from all the stills pass into these pipes, which convey them ultimately into the store-tanks for each fraction. Care must be taken that the pipes *h h* have sufficient fall, and that the later distillates are not too much cooled in them, which would be sure to stop them up with naphthalene, etc. Such

cooling is partly prevented by covering the pit over with planks; but it is safer to put steam-pipes into the pipes conveying the later distillates. A special tap in the bottom of the collecting-box *e* permits samples to be taken and the contents to be run off at will. It is also possible to adapt this box to a continuous separation of the ammoniacal liquor; but this is an unnecessary complication, and it is more advisable to let this separation take place in the receivers. One of the taps must be connected with a pipe leading back into the tar-pits, or into a special small tank, to receive the tar when the still is boiling over.

A similar arrangement is shown by Engler (*loc. cit.*), and is

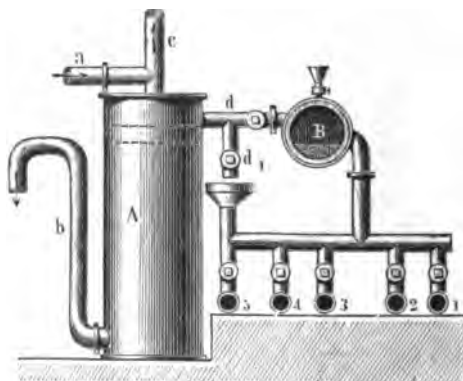


FIG. 105.

represented in Fig. 105. The oil and water run through *a* into the cylinder *A*, where they separate. The water runs off through *b*; the gases escape through *c*; the oil runs through *d* into the "lantern" *B*, where the glass pane permits observing its colour, etc. From this point the oils are carried on through the taps 1 to 5 to the different receivers; the last, and heaviest, oils do not pass through the lantern, but straight into No. 5 through the tap *d*<sub>1</sub>. This apparatus, which is used in refining petroleum, would require some modifications if it were to serve for distilling coal-tar.

The *receivers* or *store-tanks* for the various fractions may be of any shape—square, cylindrical, etc. They are always made of wrought-iron, and should be very well riveted and caulked; otherwise, especially if placed on the ground or even under-

ground, great losses by leakage may occur before anything is noticed, which may even seriously contaminate neighbouring wells and watercourses. Even a previous testing with water will only reveal coarser leaks, since tar-oils penetrate much more easily through the joints than water. Hence the store-tanks must be closely observed for some time; if they are sunk in the ground there must be a free space left all round them for some days after they have been first taken into use, so that any leaks may be detected and stopped before the earth is filled in. The bottom of the vessels ought always to be formed of one piece. Of course the needful precautions against corrosion by rusting must be taken.

Light oils are best kept in closed cylinders, heavy oils in open tanks, from which the solid naphthalene or anthracene crystallizing out can be easily removed.

At some works, steamboiler-shaped cylinders (either horizontal or upright), which can be also used for *forcing-up the oils by compressed air (montejus)*, are preferred as receivers, or at least as store-tanks. Instead of pumping the liquids by means of ordinary pumps, which is very inconvenient in the case of tar-oils, owing to the impossibility of employing fatty or india-rubber packings, they are now usually pumped by air-pressure, compressed air being conveyed from an air-pump or blowing-engine to every one of the receivers. This air presses on the surface of the oil and forces the liquids through ascending pipes, which reach down to the bottom of the vessel, and are provided with stopcocks, to any suitable height or place. Hence the moving parts of the machinery are nowhere in contact with the oils.

*Explosions by the employment of air-pressure for moving tar oils* have been observed by Klocke (*Chem. Zeit.*, 1905, p. 725). This happened in several cases where hot oils, serving for the extraction of benzol from coke-oven gases, were repeatedly moved about under a pressure of from 2 to 4 atmospheres. The cause of this seems to be the gradual formation of sulphurets of iron, which may inflame already at a temperature of 120° or 123° C. This has caused many factories to abstain from the use of air-pressure for that purpose. If the air contains at least 12 or 13 per cent. CO<sub>2</sub> (say, in the shape of cold combustion gases), no such danger would exist.

Specially constructed receivers for stills working under a *vacuum*, and for the *pitch*, where it is run off in a very hot state, will be described lower down.

*Treatment of the Gases escaping from the Condensers.*

We have already mentioned the permanent gases formed in the distilling process. They are partly combustible; but it will hardly ever pay to utilize them as fuel, especially as that would entail considerable danger of fire. Even when they are much cooled, these gases at first carry away some of the most volatile of the tar-oils mechanically. Moreover, they contain sulphuretted hydrogen, ammonium sulphide, carbon disulphide, perhaps carbon oxysulphide, and other noxious gases, which may at times give rise to complaints of nuisance. Detailed observations on this subject are described in the *Alkali Inspector's Report for 1897*, p. 35. So long as the distillate contains water, there is but little  $\text{H}_2\text{S}$  in the gases, the smell of  $\text{CS}_2$  and of  $\text{NH}_3$  predominating. When the water ceases to appear, the smell of  $\text{H}_2\text{S}$  increases, and later on the gases have much heating-power. Towards the end of the process vapours of a very offensive and irritating kind are evolved, which are not completely condensed. Hence it will sometimes be necessary to subject the gases to a purifying process. An apparatus for this purpose, substantially as employed at a large London tar-works, is shown in Figs. 106 and 107. The gas-pipes of all the cooling-worms are connected with a main pipe, which ultimately descends at *a* and enters the box *b c*. This is divided into two parts by a partition, *d*, which does not reach quite to the bottom. The compartment *b* is empty, with the exception of a little water at the bottom, which is kept level with the lower edge of the partition *d* by means of the overflow-pipe *e*. The compartment *c* is filled with coke or some other material presenting a large surface, and constantly moistened with water by means of the perforated cross-pipe *f*. This compartment serves as a scrubber: the gas is washed by the water; and at the same time the oily parts are condensed owing to the speed of the gases slackening, to the friction upon the surface of the coke, and the rinsing action of the water. It seems preferable to assist the division of the gas into many jets by nicking out the lower edge of the partition, *d*, as shown in

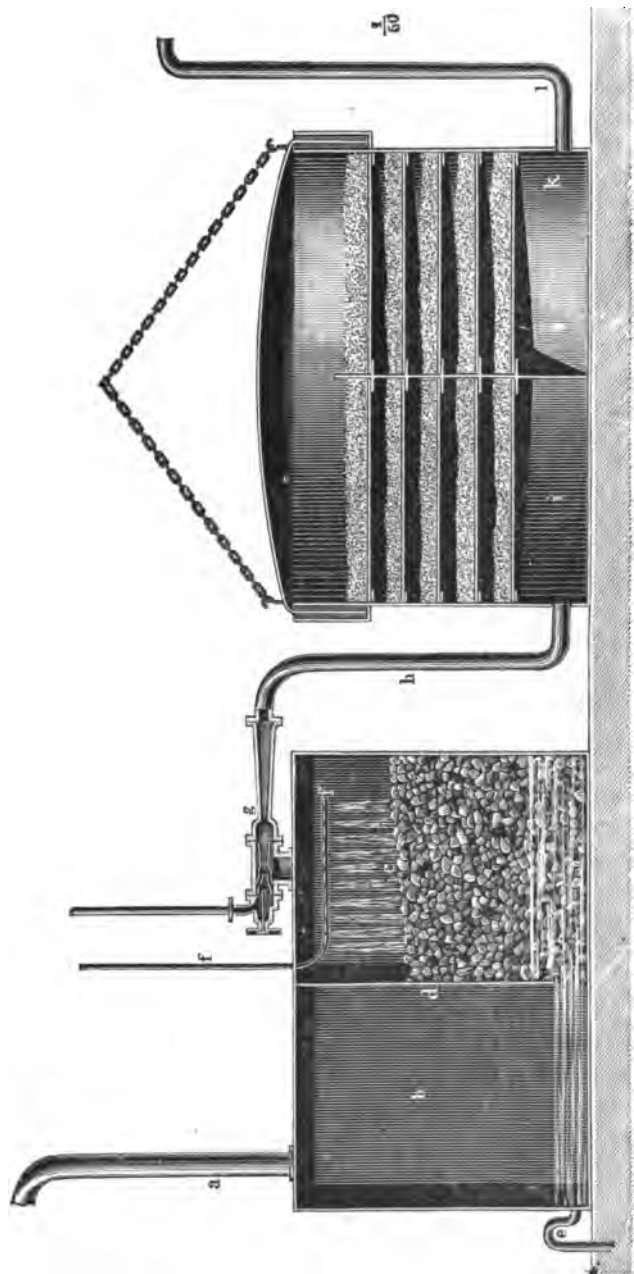


FIG. 106.



Fig. 107. In most cases the gas will be allowed to escape by means of a pipe put on the top of *c*, either into the open air or into a chimney; only provision must be made for preventing the water in *b* from rising quite up to the partition *d*, so that the gas can pass through. But where it is desirable to prove to outsiders that no precaution against nuisance has been neglected, a further purifying-apparatus is added, say an oxide-of-iron purifier (*i k*), from which the gas escapes at *l* into a chimney-flue. This purifier is exactly like those used at the gas-works, but on a much smaller scale. If the washing in *c* is to be made especially efficient, the gas is forced right through the water by means of an injector (*g*), which takes it through

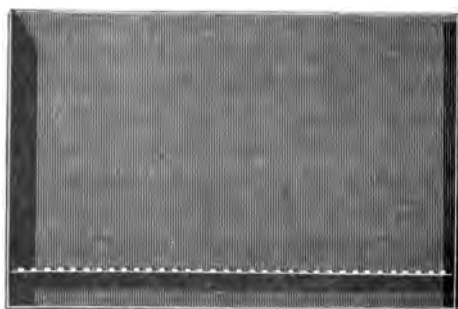


FIG. 107.

*h* to *i*. The liquid hydrocarbons are all retained in the vessel *b c*; the sulphuretted hydrogen is absorbed in the purifier *i k*; and the last remnant of the smelling gases is made innocuous in the hot fire-flue into which they pass.

Another arrangement for avoiding all nuisance by the use of a vacuum, as devised by Mr S. B. Boulton, will be described later on, when treating of the vacuum process.

According to the *Alkali Reports*, 1893, p. 20, the gases can be aspirated from the end of the worm by an injector or fan-blast, and passed through a water-lute into a fireplace, or else underneath a grating placed in a brick-pit, oxide of iron being put on top of the grate.

Another plan is: blowing the gases into a brick-lined pit, covered by a grating on which a layer of ferric oxide is placed, which is easily turned over from time to time. A light, open, wooden shed protects it from the rain.

In case the stills are worked with a vacuum, the gases issuing at the end are made to pass through a column fed with tar-oil (for retaining oily matters), and through sulphuretted hydrogen purifiers before escaping into the atmosphere.

If (as happens sometimes) one set of condensers acts for two or three stills, there is a possibility of noxious gases getting from this condenser into an empty still which men are busy cleaning. They might be suffocated thereby, and that arrangement must be therefore altogether condemned.

Rambousek, in the ninth volume of the *Zeitschrift für Gewerbe-Hygiene*, published at Vienna, reports on the injurious action of those gases on the respiratory organs, and on the "tar- and paraffin-itch" or "acne" caused by the action of the tar.

A very important paper on the noxious vapours from tar-distillation is that of Craven and Coleman.<sup>1</sup> We quote the most salient points of it. Of the various gases escaping at the end of the condensing plant, the sulphuretted hydrogen is that which is most easily subjected to accurate estimation, and it is probably also the most important in the question of "nuisance." It appears at two periods; in the beginning, where from 5 to 10 grains  $H_2S$  per cubic foot is present, and again from the commencement of the light-oil stage up to the end; during this time its proportion regularly increases, beginning with 10 and ending with 112 grains per cubic foot. The most usual way of dealing with it (where this is attempted at all) is to draw it through a water-seal and then pass it underneath a fire, *e.g.* the steam-boiler fire. Even if all  $H_2S$  is burnt here (which is frequently not the case), it is converted into another noxious gas, *viz.*,  $SO_2$ ; this may injure the boiler plates, and sometimes explosions have occurred from this cause, when the action of the aspirator was disturbed in some way, and the fire flashed back through the water-seal. This method, therefore, ought to be entirely abandoned. Another, much practised, method is the application of absorbing media in "dry purifiers" (*vide supra*, p. 432). When employed in the ordinary manner, drawbacks are caused in this process principally by the action of the carbon disulphide. The authors therefore attempted to solve the task by the employment of "wet purifiers." They force the gas by means of an air-pump (which they prefer to an exhauster as being more reliable) through an absorber, charged with milk of lime and sulphate of iron, and therefore containing hydrated oxide of iron, and after distilling a batch of 40 tons tar, they pump air through the absorber during an hour, which is quite

<sup>1</sup> *J. Soc. Chem. Ind.*, 1901, p. 200.

sufficient for revivifying the absorbing agent. Of course this becomes gradually inactive, but experience had shown that 1 cwt. of lime and 2 cwt. of sulphate of iron in 200 to 300 gall. of water suffice for about 400 tons of tar. The gas issuing from the absorber has a slight odour, caused by hydrocarbons, which might be dealt with by a second absorber, charged with heavy tar-oil. For a complete plant they propose to send the gases first to a coke scrubber, where a very small stream of water would absorb the ammonia, then through an absorber fed with high-boiling tar-oil, where carbon disulphide and hydrocarbons would be retained, then through an absorber containing a mixture of water, sulphate of iron and lime, and at last through another absorber, containing the same mixture, or else milk of lime only. The pump, of course, is placed at the end of the whole set. Sometimes free sulphur is deposited in front of the coke scrubber, which can be dealt with before the gases reach the scrubber.

When this paper was published, there had not been sufficient experience gained to declare the process as absolutely successful in all respects, but it seems the best as yet proposed.

#### *Working of the Tar-stills.*

The stills are *charged* with fresh tar while they are still hot from the last operation, but not so hot that they might suffer damage from the cold tar—that is, a few hours after running off the pitch. The tar is either pumped in directly or run in from a higher tank previously filled. In both cases the bore of the feed-pipe is wide enough for the charging not to take too much time, say 6 in.; the air escapes not only through the condensing-worm, but also by an air-cock or by the overflow-cock, *s.*, Fig. 90, p. 411. The latter also makes any other gauging of the contents of the still unnecessary. Where it is absent, the level of the tar must be ascertained by a float, or by a gauge-rod introduced into a hole, afterwards closed by a screw-plug. The stills may be filled up to the point where the cylindrical part merges into the dome-shaped portion. Watson Smith states the permissible level at 9 to 12 in. below the manhole—with thin tars, 18 in. below the same. This is not a sufficient indication, as the manhole is not always placed at the same height. We may better state the case thus: that the space

between the overflow-cock and the still-top should be 24 to 30 in., and in semi-globular domes 36 in.

All the openings are now closed and the firing is commenced. The *heating-up* may even be begun when the still is only half filled, as the level of the tar is then above the flues; although the air-cock or overflow-cock is then open, no loss is incurred, because the heating-up of the large bulk of tar takes much time, and the new tar running in causes a constant cooling. Care must be taken to see that the worm is not *choked up*, which sometimes happens in the following way: after the close of the previous operation the distillation slowly continues, whilst the water in the condensing-cistern cools down, so that "green grease" accumulates in the worm; this can usually be cleared out by blowing steam through the worm. At some works the state of the worm is tested by running a little water through it before commencing the work. As soon as the charge is all in the still and the openings are closed, the fire is increased; and this is continued up to the point at which the distillation is about to commence. This will occupy more or less time, according to the size of the still and the season; with small stills (5-ton charge) it requires about two hours, with large ones (20- to 25-ton charge) it takes five hours in summer, six hours in winter. One or two hours after the commencement of firing, the tar begins to rise and froth; and now the greater part of the ammoniacal liquor can be run off by the overflow-cock. After this the firing must take place somewhat more cautiously, to avoid sudden boiling-over, which might otherwise happen with the violence of an explosion. From this time up to the beginning of the distillation the fireman should be always in his place and must watch the worm. As soon as the first drops appear at the end of the refrigerator, he must open the fire-door and slacken the fire; for now the danger of *boiling-over* is greatest. With proper management of the still this need *never* occur (excepting the case of tars containing too much water, which ought to be previously removed, as shown on pp. 384 *et seq.*, or too much free carbon, see lower down); but if it does take place it is little use opening the fire-door, letting down the damper, etc., because the mass of heat stored up in the tar, the iron, and the brickwork is too great; even completely drawing out the fire (which can only be done where the still

is quite isolated) does not act instantaneously. But it does good to pour cold water on to the still-top; and the same means must be resorted to whenever for any reason the distillation has to be stopped as quickly as possible. When working with properly dehydrated tar, none of these precautions will be needed, and much time is saved as well.

The following are signs that the distillation is about to begin:—Vapours issue from the end of the cooling-pipe, often in puffs, and gradually drops are condensed from them. The still-head gets warm, and the worm also where it is not yet covered by the cooling-water. Now in any case the fire must be slackened, for the distillation will commence directly. This is still more necessary as soon as a continuous jet of liquid comes out of the worm; it is then time to open the fire-door, or, what is better, to let down the damper. If at this stage there is any excess of heating, the ebullition takes place with violent bumping and frothing-up, and in the worst case the mass suddenly swells up and boils over.

The tendency to eruptive ebullition was formerly attributed entirely to the *water* contained in the tar, and was believed to be all the greater the more water is present. It has already been mentioned how the quantity of water, and with it the bumping and frothing, can be diminished.

Köhler (*Z. angew. Chem.*, 1888, p. 677) states that the boiling-over of tar-stills is in the majority of cases caused by an excessive percentage of *free carbon*, which causes the vesicles of gas and vapour to adhere to the carbon particles, and thus greatly swells the volume of the tar. Whilst tars with 12 or 15 per cent. free carbon, even when containing much water, distil quite normally, other tars containing 20 to 28 per cent. free carbon show a strong tendency to boil over. Kraemer (priv. comm.) entirely objects to this opinion; tar rich in carbon retains the water more pertinaciously, and is separated from it less easily. The presence of *gases dissolved in the tar* also increases that tendency.

The following proposals have been made for preventing the boiling-over of tar-stills. Luhmann places below the top pipe a lenticular wrought-iron vessel (Fig. 108), provided with an

outlet-pipe carried outward, and a pipe connecting its top with a water-reservoir. When the attendant notices a swelling-up of the tar, he should open the water-tap; the top part of the still is thereby cooled, and the condensing liquid, raining down upon the boiling tar, breaks up the froth. Later on Schroeder patented the same arrangement (Ger. P. 76366). H. Kropff (Ger. P. 55933) removes the froth by blowing cold air on to the surface of the boiling liquid.

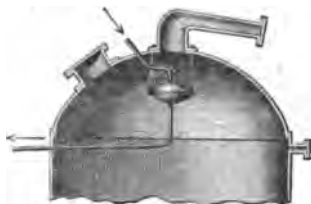


FIG. 108.

Other arrangements for breaking up the froth of liquids boiling in a vacuum are described by C. Heckmann (Ger. Ps. 51701 and 70022) and P. Neubäcker (Ger. P. 110972).

Le Clercq's Patent Gesellschaft zur Fabrikation von Teer- und Dachpappen-Maschinen (Ger. P. 166723) describe a system claimed to be safe against fires and boiling over. A system of heating-coils, a closed tank, and a pump are connected in such manner that only the contents of the coil can get into direct contact with the fireplace, thus enabling the heating of the tar, without danger of fire, to much higher temperatures than is otherwise possible.

Ostreijka (*Nafta*, 1908) treats tar containing water, and therefore inclined to boiling over, with superheated steam, gradually going up to the melting-point of tin ( $228^{\circ}$ ).

A. Spilker (*Kokerei, etc.*, p. 43) states that all those attempts at preventing the boiling over of tar are very unsatisfactory. It is decidedly preferable to dehydrate the tar in special stills as much as possible, and only then to submit it to distillation. This proceeding gives the best results, and is usually applied in well-conducted factories.

During the first period of the distillation *permanent gases*, water (containing ammonium compounds), and the most volatile tar-oils are given off, which always carry along some of the less volatile constituents, partly in consequence of the vapour-tension of the latter, partly mechanically. All this time the cooling-tank must be well supplied with cold water, both for condensing the tar-oils and because the condensation of the steam and ammonia liberates much heat. A 1-in. water-pipe and 15-ft. head of water will supply a cooling-tank for a 20-ton still.

*Fractions.*—At British tar-works usually the *first fraction* is that portion of the oils which comes over along with water; so that the first receiver contains both ammoniacal liquor and tar-oils. The latter are called first runnings, first light oils, crude naphtha, etc. Water will form a greater or smaller proportion of the distillate, according to whether it has been previously removed or not; this proportion is ascertained by catching some of the distillate in a glass cylinder, in which naphtha and water separate at once, the former floating on top of the water. At first much water and little oil comes, then less water and more oil; occasionally the time when the water ceases to come over can be somewhat accurately fixed for changing the receiver. But it is safer to wait till the distillation slackens. This is called the “break,” and is probably caused by the fact that the aqueous vapour carries along a quantity of oils of much higher boiling-point than that of water; so that, after all, the water is removed first. The temperature has to rise a good deal before the liquid begins to boil anew. At this stage, often for two hours, hardly anything comes over but a little water; and, from the peculiar noise made by the steam within the still, this period is sometimes called the “rattles.” The cause of the rattles is the falling-back into the contents of the still of the last portions of water which had been vaporized and had been condensed before getting into the worm. When coming in contact with the tar, now heated considerably over  $100^{\circ}$ , it is instantaneously re-vaporized with a somewhat explosive force, and thus the rattling or crackling sound is produced. The same phenomenon is often observed when distilling, in the laboratory, naphtha containing traces of moisture. The rattling noise ceases when the temperature has risen high enough; and the distillate then comes over in a thick, quiet stream. It is now mostly collected in another receiver as “light oil” or “second light oils.”

The ceasing of the appearance of water is not by itself a sufficient signal for changing the receiver; for sometimes a little water comes off along with the light oil, and even, at first with the heavy oil, owing to the hydration water of phenol. Hence other signals must be the smell, the specific gravity, and the quantity of the distillate, or else the indications of the thermometer. The smell, which of course cannot be very well

defined, generally indicates to the attendant quite clearly when he must change the receiver for light oil: the first runnings smell much more pungently than the light oil; and the transition is pretty sharp. The specific gravity increases slowly, and does not in this case give a very distinct guidance.

Of course the *specific gravities* of the various oils must not be compared at different temperatures, but must be *reduced to the ordinary temperature, e.g.*, by placing the hydrometer vessel (which for factory purposes is best a *lead* cylinder, not a glass jar) into a bucket filled with cold water, until the temperature has gone down to 20° C., which in the warm season takes some time. To save this, Peterson-Kinberg gives the following table, showing the specific gravities at various degrees C. :—

80°	70°	60°	50°	40°	30°	20°
...	...	0.96	0.97	0.98	0.99	1.00
...	...	0.987	0.998	1.009	1.019	1.029
...	1.005	1.013	1.018	1.025	1.035	1.045
1.01	1.02	1.03	1.038	1.05	1.06	1.07
1.02	1.03	1.04	1.048	1.06	1.07	1.08

For reducing the specific gravity of any tar-oil to the normal temperature, Church (*J. Ind. Eng. Chem.*, 1911, p. 232) employs the factor 0.0008, by which the number of degrees above the normal temperature is to be multiplied, the product being added to the specific gravity found at higher temperatures. *Cf.* also later on the reducing-table of Shipley, given for pickling-oils.

If the fractions are to be made according to the indications of the thermometer fixed in the still (p. 417), it is usual to change at the following points :—

1. First runnings, up to 105° or 110° C.
2. Light oil, up to 210°.
3. Carbolic oil (for phenol and naphthalene), up to 240°.
4. Creosote oil, up to 270°.
5. Anthracene oil, above 270°.

These points are, of course, not always the same, partly because the thermometers do not reach down exactly to the same depth. The German tar-works mostly do not separately collect "first runnings," but make the fractions in the following way :—

1. Light oils, up to 165° or 170°.
2. Middle oils (for carbolic acid and naphthalene), up to 230°.
3. Creosote oil, up to 270°.
4. Anthracene oil, above 270°.



Girard and Delaire (*loc. cit.*, p. 10) quote the following fractions :—

- |                     |      |              |         |                |
|---------------------|------|--------------|---------|----------------|
| 1. Huiles légères,  | from | 30° to 140°, | sp. gr. | 0.780 to 0.850 |
| 2. Huiles moyennes, | "    | 150° " 210°, | "       | 0.830 " 0.890  |
| 3. Huiles lourdes,  | "    | 220° " 350°  | "       | 0.920 " 0.930  |

(The specific gravities are evidently wrong, and, no doubt, again prove an unaccountable confusion with paraffin oils.)

The following special observations have been made by H. Köhler with a 15-ton still, worked in a regular way up to medium-hard pitch, with a vacuum. The specific gravities were taken at 15° C. for the lighter fractions, at 30° C. from carbolic oil upwards. The tar distilled weighed 15,000 kgs.

Time of sampling.	Temp. in the still-head.	Ammoniacal liquor.		Oil.		Quality of distillate.	Total quantity of distillate.
		Volume per cent.	Specific gravity.	Volume per cent.	Specific gravity.		
8 A.M.	80	40	1.080	60	0.878	First runnings.	880 kilog. aqueous liquor; 440 kilog. oil; sp. gr. 0.925.
10 "	92	57	1.020	43	0.891		
12 NOON.	95	60	0.990	40	0.892		
2 P.M.	96	63	0.995	37	0.893		
4 "	97	65	0.996	35	0.897		
6 "	97	70	0.999	30	0.901		
8 "	98	80	1.000	20	0.902		
10 "	98	75	1.000	25	0.905		
12 MIDN.	98.5	70	1.000	30	0.905		
2 A.M.	98	70	1.000	30	0.910		
4 "	98	65	1.000	35	0.917		
6 "	98	60	1.002	40	0.922		
8 "	98	50	1.005	50	0.923	Carbolic Light oil.	520 kilog.; sp. gr. 1.015.
10 "	98	30	1.050	70	0.950		
10.30 "	167	6	1.095	94	0.960		
11 "	220	...	...	100	0.980		
11.30 "	223	...	...	100	1.000		
12 NOON.	230	...	...	100	1.010		
12.30 P.M.	239	...	...	100	1.015		
1 "	240	...	...	100	1.023		
1.30 "	252	...	...	100	1.025		
2 "	255	...	...	100	1.029		
2.30 "	263	...	...	100	1.035		
3 "	265	...	...	100	1.040	Cresote oil.	1800 kilog.; sp. gr. 1.044.
3.30 "	269	...	...	100	1.049		
4 "	278	...	...	100	1.057		
4.30 "	280	...	...	100	1.065		
5 "	285	...	...	100	1.086		
5.30 "	285	...	...	100	1.095		
6 "	290	...	...	100	1.099		
6.30 "	285	...	...	100	1.0995		
						Anthracene oil.	1450 kilog.; sp. gr. 1.005.

In the case of tars of known quality, the time and the quantity of the distillate are among the most important signals for changing the receivers. The former varies of course with the size and even with the shape of the still, its setting, etc. We shall make some statements regarding this subject and the quantity of the different fractions at the end of this chapter. The quantity of the distillate can only serve as a guide where every still has its own receivers, which is rarely the case at large works.

Attempts have been made to greatly increase the number of fractions at the first distillation of coal-tar, with the view of better isolating the products therefrom. All such attempts have hitherto failed, and probably will continue to do so in future. In no case are pure products obtained, and hardly any of the subsequent rectifications are saved; so that the whole is but a superfluous complication of the process. This is founded on *the nature of fractional distillation*, which has been cleared up by a number of researches.<sup>1</sup>

The various components of a mixture do not distil simply in the order of their boiling-points, not even taking into account the vapour-tension of the substances not yet arrived at their boiling-point; but their vapour-density must also be taken into account. According to Dossios and Wanklyn, the quantity of each component distilling at a certain temperature is found by multiplying its vapour-tension at the boiling-point of the mixture by its vapour-density, or, what comes to the same thing, its molecular weight. Thus methylic alcohol (molecular weight = 32) boils at 66°, methylic iodide (molecular weight = 142) at 72°; but from a mixture of the two, more of the latter distils over. A mixture of 91 parts carbon disulphide (boiling-point 47°) and 9 parts alcohol (boiling-point 78°) boils constantly at 43° to 44°, and during distillation retains its composition. Hence the liquid possessing the highest vapour-tension does not necessarily distil most rapidly; for what its companions lack in tension they may make up in vapour-density. If the tension is called  $t$ , the vapour-density  $d$ , we have for different liquids

<sup>1</sup> Dossios, *Jahresber. f. Chem.*, 1867, p. 92; Wanklyn, *Phil. Mag.* (4), xlv., p. 129; Glashan, *ibid.*, p. 273; Naumann (*cf.* below); Thorpe, *J. Chem. Soc.*, 1879, xxxv., p. 544; F. D. Brown, *ibid.*, p. 547; 1881, xxxix., p. 304; Konovalow, *Ber.*, 1881, pp. 2224 and 2678, etc.

$x = ktd$ , in which formula  $k$  is a constant to be found by experiment in every single case. If the vapour-densities and tensions are inversely proportional to each other, and the values of  $k$  are equal, the products  $k_n t_n d_n$  will all be the same; *i.e.*, the mixture will remain unchanged throughout the distillation. For this reason homologous series (*i.e.*, those whose members differ from each other by  $\text{CH}_2$ ) are not easily separated by fractionating; for whilst the vapour tension is lowered by each  $\text{CH}_2$ , the vapour-density rises. This explains why so many substances distil more quickly in a current of steam; for aqueous vapour is one of the lightest bodies. By diminishing the pressure the difference between the vapour-tensions of different liquids is increased, whilst their vapour-densities remain the same;<sup>1</sup> hence, according to some, they are more easily separated, as is proved by the success of exhaustion in gas-making and tar-distilling (see below). But to this it has been objected that the lowering of the boiling-points, caused by producing a more or less complete vacuum, does not in reality facilitate the separation of the various fractions, the differences in their boiling-points remaining practically unaltered.

A mixture of two liquids which are not mutually soluble, on distillation, exhibits a boiling-point below that of the more volatile substance. A mixture of carbon disulphide (boiling-point  $47^\circ$ ) and water boils at  $43^\circ$ , etc. This observation has been generalized by Naumann,<sup>2</sup> who found that the boiling-point of such a mixture is constantly below that of the most volatile component—and also that the proportion of substances is always the same, *viz.*, equal to the proportion of the vapour-tensions of the two components, measured at the temperature of boiling, multiplied by their molecular weight. This behaviour is of importance in tar-distilling also, where water boils in presence of oils not miscible with it. Thus, although at  $98^\circ$  the vapour-tension of naphthalene is only 20 mm., that of water 712 mm., yet at that temperature 49.4 g. of water pass over with 8.9 g. of naphthalene.

It is hardly necessary to mention that the different fractions are not divided by any sharp lines, and that at different works they are taken differently. In some places no distinction is

<sup>1</sup> Winkelmann, *Poggend. Annal.*, N.F., i., p. 430.

<sup>2</sup> *Ber.*, 1877, p. 1421; 1879, pp. 2014, 2099.

made between first runnings and light oils, but all the distillate having a specific gravity below 1.0 is taken as crude naphtha. The subsequent treatment must be adapted to this.

#### *First Fraction.*

In any case *first runnings* and (aqueous) *ammoniacal liquor* come together, the former floating on the latter. The latter is worked up like any other similar liquor, as will be described in the second part of this book. The two liquids at once separate sharply; the water is either pumped away from below, or is continuously carried away by a pipe starting from the bottom of the receiver, and turned upward; or else the same object is attained by a partition reaching nearly to the bottom of the receiver, or in some other way.

#### *Light Oil.*

The *second fraction* (if the distillate coming over before the carbolic oil is, as usual, divided into two fractions) begins after the "break," when the distillation proceeds quite smoothly, in a full stream and without any further danger of boiling over. The product is no longer a naphtha, but has a more oily nature; it is called either "light oil" or else "second light oil," or "second runnings." We shall in future use the first name in this restricted sense. This fraction is usually continued up to the point where its specific gravity is equal to that of water. The men run a few drops into a cylinder partly filled with water; if the oil floats anywhere within the water in single large, globular drops, its specific gravity is = 1.0 (the average specific gravity of the light oil passing over up to this point ranges from 0.910 to 0.950) and it is now time to change the receiver for carbolic oil. Where the fractions are made by the thermometer, this point will be about 210°. This proves that the light oil must contain a good deal of carbolic acid (boiling-point 180°) and naphthalene (boiling-point 218°); but it must be remembered that in the upper part of the still and in the still-head some cooling takes place and the vapours partly condense again; hence the principal part, especially of naphthalene, only comes over with the next fraction. But where carbolic acid and naphthalene are principal considera-

tions, the fractionation is managed accordingly. This is the object of the method of working mentioned on p. 441, where the "middle oil," passing over between  $165^{\circ}$  or  $170^{\circ}$  and  $230^{\circ}$  will comprise nearly all the phenol and naphthalene, especially if the bulb of the thermometer is not placed in the tar, but in the liquid. It is not possible to give any general prescriptions for this purpose; the temperatures in the distillation of coal-tar depend too much on the shape and size of the tar-stills, on the way they are set and on the rate at which they are driven. Large-sized stills, as shown by experience, work much better than small stills; hence the same sample of tar may give quite different results in different stills. Much more reliable for the proper fractionation is the observation of the properties of the distillates; and quite particularly the secretion of *naphthalene* from the cooled-down oils, its disappearance and especially the specific gravities of the oily distillates furnish the indications for separating the fractions.

An ample crystallization of naphthalene on cooling, *e.g.*, by letting a few drops of the distillate fall upon a piece of cold iron, is a sign that nearly all the phenol has passed over, and that it is time to change for heavy oil; for the naphthalene is much more soluble in phenols than in the indifferent heavy oils, and it will therefore remain mostly in solution in the distillates as long as it is accompanied by notable quantities of phenol, but it will crystallize out from the oils when those contain but little phenols. This rule, however, is subject to many exceptions.

During the time the light oil is coming over (that is, after the "break"), the fire is increased without any danger of boiling over, although even now for the most part a little water appears, probably owing to the hydrate of phenol splitting up. Now the cooling-water begins to get warm; but little or no fresh water is run in; so that at the end of this stage the temperature of the water surrounding the worm is about  $40^{\circ}$ . If the work is arranged for "middle oil" in the above-mentioned sense, the temperature of the water must be at least from  $50^{\circ}$  to  $60^{\circ}$ . Afterwards no fresh water at all must be run in; and sometimes even steam must be blown into the cooling-tank by means of a pipe entering at its bottom and pierced with numerous holes (*b*, Fig. 96, p. 421): this is necessary because the danger of the worm being choked up is greatest in the bottom coils. Such a

danger sets in even more near the end of the process, as we shall see later on; but it can always be provided against by allowing the water to get hot. Some English tar-distillers have not even steam-pipes in their refrigerators; but this is advisable in any case.

If the temperature in the refrigerator were kept too low, in the later period of the light oil-stage the naphthalene would crystallize and choke up the worm, thus producing a dangerous pressure in the still. The *explosions of tar-stills*, rarely as they occur, are probably always caused by neglect in this respect, either during the naphthalene- or the anthracene-period.<sup>1</sup> On the other hand, the water should not be allowed to get warm at the beginning of the light-oil stage, because then considerable quantities of the more volatile hydrocarbons are still coming over. This seems to be another reason for continuing the first fraction till benzene and all its homologues have passed over, and then condensing the "middle oil" by means of warm cooling-water.

Whether the worm is choked up, or is not, is best seen at the end of the pipe coming out of the refrigerator, where it is curved up to allow the permanent gases to be taken away. This pipe should be warm, and the liquid should run out uninterruptedly; this is readily seen when it runs into a glass jar (*c*, Fig. 104, p. 429). Where there is an intermediate vessel (*e*, Fig. 104) with cocks for the different fractions, the distillate might possibly crystallize in this, or in the pipes (*g g*) which carry away the products. This is not so very dangerous, because the whole box *e* must be first filled with crystals before the worm can be choked up; notice will be given of it by the box *e* or the cocks *f* getting cold. If the pipes *h* are sunk in the ground, are covered up, and have sufficient fall and are not too long, they will not be easily stopped up; but it is decidedly advisable to be prepared for that contingency by making provision for blowing steam through them.

Where the work is carried on with evacuation by an air-pump or an injector, in the manner to be described hereafter, there is absolutely no danger of any choking-up of the worm. But

<sup>1</sup> A frightful explosion occurred in this way at a tar-works near Gateshead-on-Tyne, in 1886, by which several people were killed, among them the managing partner. The tar-stills were not provided with safety-valves.

in any case the stills ought to be provided with a safety-valve or an equivalent contrivance (pp. 416 *et seq.*).

J. Vaughan<sup>1</sup> proposes preventing explosions which might occur, in consequence of the worm choking-up, by means of a wide pipe reaching nearly to the bottom and passing out at the top, connected with a large empty cylindrical boiler placed near the still and at a lower level. The connecting pipe is enlarged at the highest point, and is there closed by a valve kept down by its own weight. The whole of the pipe is kept warm. If any excessive tension should occur within the still, the tar will rise in the pipe, lift the valve, and flow over into the empty cylinder.

#### *Carbolic Oil.*

The distillate at and above the specific gravity 1.03 or 1.04 was formerly not fractionated at all, but collected all together as heavy oil, dead oil, or creosote oil, and sold for pickling timber, without any further manipulation. Only exceptionally could the first and the last portion of the creosote oil be separately sold, the former for carbolic acid, the latter for lubricating-grease. When carbolic acid was specially aimed at, there was but rarely a special fraction made for it; the light oil was only driven a little further. No doubt phenol and its homologues, as we shall see in Chapter IX., occur also further on in the heavy oil, and constitute part of its value for preserving wood; but making pure phenol from proper heavy oil is rather difficult and expensive, and only takes place exceptionally. For this reason, since large quantities of phenol have been required for the manufacture of colours, for disinfecting, and for medicinal purposes, it has become usual to make a special fraction containing as much carbolic acid as possible and with it a great deal of naphthalene. Although the boiling-points of these compounds are widely apart (180° and 218°), a large quantity of naphthalene is carried over below its boiling-point, and, on the other hand, phenol is kept back in the tar-oils above its boiling-point. Where no thermometer is placed in the tar-stills, this fraction is made to commence whenever the specific gravity of the distillate is 1.0; moreover, its yellower colour and its smell serve as guides. A certain quantity of

<sup>1</sup> *Engineer*, 1880, v., p. 298.

the oil now passing over is received as "carbolic oil"; and when this quantity has come over, the change for creosote oil is made. The amount of carbolic oil is usually 100 gall. from a charge of 2000 to 2500 gall., *i.e.*, 4 or 5 per cent. of the tar. Ordinary Lancashire tar gives 5 per cent. by volume of good crude phenols, yielding 65 per cent. (by volume) of a carbolic acid, sufficiently pure to crystallize at ordinary temperatures with ease (Watson Smith, *J. Chem. Soc.*, 1886, vol. xlix., p. 21).

Where it is preferred to consult the thermometer, at some works the fraction passing over between  $210^{\circ}$  and  $240^{\circ}$  is taken as carbolic oil (probably with the bulb of the thermometer dipping in the liquid itself), whilst at other (very large and well conducted) works the "middle oil" is received between  $170^{\circ}$  and  $230^{\circ}$ . The latter course seems most worthy of being recommended, as it leaves a suitable margin below the boiling-point of phenol and above that of naphthalene. Where "prepared tar" for the manufacture of roofing-felt is made, it is usual to stop the distillation at  $210^{\circ}$ , and run the now remaining contents of the still into the receiver.

If the oils on cooling show a large crystallization of naphthalene, this is a sign that most of the phenol has already come before, or that it is now time to change for creosote oil; for (as mentioned *supra*) naphthalene is much more soluble in phenols than in the heavy indifferent tar-oils, and hence mostly remains dissolved in the distillate so long as there are considerable quantities of phenols present, but crystallizes in large masses on cooling when the phenols are becoming scanty; but this rule is not without exceptions.

Every factory must, of course, ascertain for itself which are the proper limits of this fraction; they will depend upon the size and contents of the stills, the position of the thermometer, the quantity of the tar, etc. The criterion is that the crude carbolic acid, obtained by the subsequent treatment of the carbolic oil, is of the proper quality, as will be explained in Chapter IX. So far as naphthalene is concerned, enough of it is sure to come over, and sometimes it crystallizes out in large quantities. Only exceptionally does tar contain so little naphthalene that it is not partly separated in the solid state. Hence the previously mentioned precautions for preventing



the choking-up of the pipes should be always observed in this case.

*Creosote Oil.*

The fraction which comes over after the carbolic oil generally contains at first sufficient naphthalene for some of it to crystallize on cooling in a shallow dish. But after some time this ceases; the naphthalene, still present, but in smaller quantity, remains dissolved in the liquid hydrocarbons even after cooling; and as phenol and its homologues, which impart to the products the property of promoting friction, have ceased even before, the portions now received possess a milder, more oily or greasy nature, which makes them suitable for cart-grease. Hence this product is frequently called "soft oil," or "liquid creosote oil." It generally begins to appear when about half of the heavy oil (calculating for a distillation up to hard pitch) has been received. Before an industrial use had been found for the anthracene oil, the second half of the heavy oil, *i.e.*, the "soft oil," along with the "red oil," or anthracene oil, was sometimes run into a special receiver as "grease oil," and the liquid soft oil was occasionally separated from the butter-like grease. This was done chiefly in the first years after 1860, when, owing to the American civil war, the price of rosin had risen enormously, and the cart-grease-makers were glad to get any substitutes for rosin-oil; and this is now again done at some tar-works. The liquid soft oil is often called "yellow creosote," from its yellowish-green colour, which, however, soon changes into dark brown. Its value as a lubricant is inferior to that of the last portion, the "solid creosote," or a green grease answering to what is now called "anthracene oil." In any case these products are very much inferior as lubricants to rosin-oil or lubricating oils from petroleum and paraffin-oil refineries. The separation of yellow from solid creosote is now principally made for the purpose of obtaining, in the "*anthracene oil*," that constituent of coal-tar (*viz.*, anthracene) which, since Graebe and Liebermann's discovery of artificial alizarin (1868), has become by far the most valuable product of this industry. All the remaining heavy oils are put to the uses described in Chapter VIII.

Since the tar made at the Scotch gas-works contains too

little carbolic acid and anthracene to make it worth separating, most of the Scotch tar-distillers do not make the fraction here described, but collect all the heavy oils together for pickling timber.

### *Anthracene Oil.*

The beginning of the anthracene-oil period is either judged by outward marks or by the thermometer, sometimes by the quantity of the distillate. Usually it is assumed that about one-sixth of the heavy oil (beginning from sp. gr. 1.105 up to 1.14, up to hard pitch) comes over as anthracene oil; but in some cases as much as one-half of the heavy oils is collected as anthracene oil. The latter may be reckoned to begin when the oil ceases to remain liquid after complete cooling—that is, when a fresh separation of solids sets in. Where the thermometer is employed, 270° is nearly everywhere assumed as the commencing-point. Probably this general consent results from the fact that from this stage the thermometer-bulb is always in the vapour. Sometimes first and second “green oil” or “red oil” are received separately.

### *End of the Distillation.*

Formerly this was decided according to whether hard or soft pitch was to be left in the still. Sometimes, but rarely, the work was stopped as soon as all the light oil had passed over; the residue then remaining in the still was called “asphalt” (in French, *brai liquide*), and employed in the paving of streets, for protecting underground iron tanks from corrosion, for the manufacture of roofing-felt, and similar purposes (see next chapter). But the work was nearly always continued further, either up to soft pitch or hard pitch (*brai gras* and *brai sec*). Soft pitch is obtained when rather more than half the dead oil is distilled off; moderately hard pitch, when the soft oil and about a quarter of the anthracene oil are taken away; hard pitch, when the distillation is carried to its conclusion, as will be described presently. The special characters of these different descriptions of pitch will be given in the next chapter.

Since anthracene has become the most valuable product of tar-distillation, wherever the tar is not very poor in anthracene,

the distillation is mostly continued till hard pitch is produced. In England and France it is frequently run out in this state; but in many English and Scotch works, and in most or all German ones, they manage differently, as we shall see.

In the last period of the distillation the water-supply to the worm-tub should be shut off altogether, the water in the tub being allowed to boil, and, if necessary, ebullition must be produced by blowing in steam.

The distillate which now separates is a mixture of anthracene, phenanthrene, carbazol, etc.; later on also of chrysene, pyrene, etc.; and ultimately contains so much of these that on cooling it solidifies in a butter-like mass which would choke up all the pipes. This must of course be avoided by keeping the worm-tub and the conveying-pipes warm, or even (more safely) by employing steam; but the best way of all is by producing a vacuum (see below). The oil running off should be about  $60^{\circ}$  C. If the distillation is continued till hard pitch is formed (*i.e.*, pitch which is hard after cooling), it becomes at last very sluggish; its cessation is determined by the manner in which the distillate solidifies and by its quantity—also by the time elapsed, and by the peculiar smell, now again changing. Steam being usually injected now (see below), the thermometer is of no further use; and in any case a mercurial thermometer could not be employed at this stage, the temperature in the interior of the still being about  $360^{\circ}$  C. In the case of tars where the distillate does not solidify, owing to its containing too little anthracene, etc., the other signs must suffice for judging when to stop. Frequently, also, the hydrometer is consulted. If the distillate shows a specific gravity = 1.090 to 1.100, the residue will be moderately hard pitch; at 1.14 it will be hard pitch; but this does not hold good of all descriptions of coal-tar, and should be tested by experiment. As soon as the distillate assumes a "gummy" state, the distillation should be stopped, for this product, although still containing anthracene, cannot be filtered at all. Under all circumstances the decisive criterion is the quantity of the distillate, from which the quality of the pitch remaining in the still may be foretold.

Köhler (*Z. angew. Chem.*, 1888, p. 677) estimates the yield of pitch beforehand from the quantity of "free carbon" the tar contains.

If the distillation is continued too long, much damage is done in several ways. In the first place, the anthracene will be too much contaminated by chrysene and pyrene. Much of the pitch is turned into coke, sometimes to such an extent that the pitch ceases to run out of the still; and even if it does run, it will not solidify in a glass-like, but in a porous, honeycombed form, which is quite unsaleable. Lastly, the still itself is much damaged by this treatment.

It should, however, be noticed that the *coking*, which is a very much dreaded trouble in the distillation of tar, is not merely a consequence of continuing the distillation too long, but it also depends upon the nature of the tar. It has been observed that tar obtained from pure coal (whether in the gas-retort or in the coke-oven) has a comparatively slight tendency to coking, but gas-tars, obtained from coal mixed with lignite, bituminous schists, and other substances of this kind, show this tendency more strongly, together with retaining water very tenaciously, and thus increasing the tendency to boil over.

E. Kopp<sup>1</sup> proposed driving off only a portion of the creosote oil and *distilling the soft pitch to hard pitch in a special still*. He asserted that he had found in such soft pitch from the Turin gas-works 4 to 6 per cent. anthracene; but this seems very improbable, and it should be remembered that at that time no exact methods for estimating anthracene were known. The pitch-still was to have a greater width than depth; the gas-pipe was to be of large bore, to join the still only 6 or 8 in. above the level of the boiling pitch, and then to bend down at once, in order to carry away more readily the heavy vapours. Towards the end the distillation was to be promoted by a current of superheated steam, or of heated air which had been passed through a red-hot pipe filled with charcoal, and thus converted into a mixture of carbon monoxide and nitrogen. During the distillation as much melted pitch as corresponded to the oil distilled was to be run into the still by means of a pipe reaching through the still-cover half-way down into the pitch; this would amount to half as much as the original charge of pitch in the still. The steam or heated gas was to issue either immediately above the surface of the boiling pitch or within the same. Lastly, when the contents of the still had become too

<sup>1</sup> Bolley-Kopp's *Spinnfusern*, p. 381.

thick they were to be expelled by the steam or air, the cooling-worm having first been shut off. We do not know whether Kopp's proposal has ever been carried out in practice. That part of it which refers to promoting the distillation by a current of steam or gas has been proposed and carried out elsewhere (see below). There remains the proposal to effect the distillation to hard pitch, not in the same still from beginning to end, but transferring the last stage to a separate vessel. This would not be very easy to do, and would not pay unless more anthracene was got out, which has not proved to be the case.

We must distinguish between this distillation of *soft pitch* up to the stage of hard pitch, and that of *hard pitch* itself to coke, which will be described in the next chapter.

In any case, as pointed out by Spilker (*Kokerei, etc.*, p. 45), the normal style of working should be to interrupt the heating from without when two-thirds of the anthracene oil have passed over, because otherwise it might happen that considerable quantities of bituminous substances would lead to a coking of the pitch. The heat accumulated in the mass then remaining in the retort, as well as the steam blown in at that stage, will complete the distillation.

#### *Distillation of Coal-tar by means of Superheated Water.*

In order to diminish the danger of fire in distilling the tar, it has been proposed to carry out the distillation, not by an ordinary fireplace, but by means of superheated water which is either circulated within the tar in strong-walled tubes, or, in the case of cast-iron stills, by tubes cast in the still mantle (Frederking's system).

This plan is not adapted to distilling tar on a large scale, as it works too slowly, but it has been introduced at some manufactures of roofing-felt by Messrs Opitz and Klotz, of Leipzig, and by the Sangerhauser Aktien-Maschinenfabrik and Eisen-giesserei. It is stated by these firms that by means of superheated water temperatures up to 400° can be attained, and that this plan is more efficient than the employment of superheated steam (see below). It has, however, not found any extensive application.

*Application of Superheated Steam in the last Stage  
of the Process.*

Apart from what would happen if hard pitch were run off too soon, the still-bottom naturally suffers considerably during the last stage of the process, when the heat has risen to a high point, especially where it is not protected by a curtain-arch. At the same time the vapours now formed, which are very heavy, cannot easily get out of the still into the worm, the level of the mass being now very low, and the upper part of the still not being heated; a portion of these vapours must condense again within the still itself; and the distillation is but sluggish. The longer it lasts the more opportunity there is for the hydrocarbons to split up into carbon and permanent gases. Hence it seems rational to promote the carrying-away of the vapours at this stage, either by superheated steam, etc., or by a vacuum, or both.

*Steam* appears to have been employed for a long time past to promote the distillation, not merely at the commencement, as described, pp. 437 *et seq.*, but again in the last stage, when it must, of course, be first *superheated*.

It is, for instance, mentioned in Cormack's patent, No. 1368, of 1864. According to Watson Smith, Mr John Barrow, in Manchester, employed steam as a secret process about the same date. I am informed by Mr S. B. Boulton that the introduction of steam is fully described by Dr Gesner in a work upon *Coal, Petroleum and other Distilled Oils*, published in London, Paris, and New York, 1865; also that Mr Boulton experimented with steam in 1865 and 1866, in conjunction with M. Audouin, and that he had used it for many years past. Steam is also mentioned in Audouin's patent of 1872 (see below), but only as a means of stirring up the contents of the still. The use of steam, however, did not become general until about 1881 or 1882. At the present time every well-appointed tar-works possesses tar-stills provided with steam; and by that means most of the troubles formerly caused by quickly destroyed bottoms, by explosions, etc., have vanished.

The steam fulfils several purposes. It assists in carrying away the vapours as before mentioned; this shortens the time required for the distillation and increases the yield: besides, it

prevents the pipes from being choked up. Furthermore (and this is of the greatest importance), the formation of hard crusts upon the still-bottom is lessened by the temperature being there kept comparatively low, and also by the agitation of all the contents of the still, so that coking and burning-on of the pitch cannot easily take place. Indeed, Trewby and Fenner assert that with the system, shown in Figs. 90 and 92 (pp. 411 and 413), no coke at all is formed on the still-bottoms, and thus cleaning out the still becomes unnecessary. At all events, the Beckton stills go for many months without cleaning. Elsewhere experience has not been quite so favourable, perhaps because the steam was introduced by a simple cross of tubes, etc.; whilst by Trewby and Fenner's plan steam ranges over every part of the still-bottom, issuing from numerous and suitably-formed outlets. For this reason we have adopted their system (introduced at the great Beckton works) in our diagrams, without undertaking any responsibility if it should be found too complicated and the outlets too liable to be choked up. Of course any similar arrangement will answer the same purpose. The arrangement described (but not illustrated by diagrams) in Audouin's patent of 1872 already consisted in projecting jets (of carbonic acid, combustion-gases, steam, and the like) in all directions, preferably downward, and near to the bottom and sides of the distilling-apparatus.

The pressure of steam employed in tar-stills usually ranges from three to five atmospheres.

A further question is: In which way is the steam to be *superheated*? At a German works the superheater is a coil of  $\frac{3}{4}$ -in. wrought-iron tubing, of a total length of 33 ft., with a bottom surface of 3 ft. 3 in. square, placed in an oven-like space above the fire-arch. The boiler-steam is first freed from liquid water in a suitable catchpot, and then enters the superheater, where it attains a temperature of 275° C. The steam-pipe, where it issues again, is covered with a thick non-conducting coating, and runs over the top of the still (which has the shape of a steam-boiler), into which it sends four branches. Each of these is provided with its own cock, and also with a special air-cock, through which the steam is blown off for a moment in order to remove any condensed water, before the cock leading into the still is opened. This arrangement has been in operation ever

since 1873, and gives perfect satisfaction. The steam is first blown in when the change is made for anthracene oil—that is, when the thermometer has got up to  $270^{\circ}$ . From this time to the end of the process no more firing is required; the heat stored up in the arch running all along the still-bottom, together with the superheated steam, suffice to finish the distillation. After the anthracene oil has been driven off, creosote oil is pumped into the still, to make soft pitch or “prepared tar” (*cf.* Chapter VI.), which lowers the temperature so far that the still can be emptied at once and recharged.

A similar system of completely dried and then superheated steam I found at another German works, employed with stills of the usual cylindrical form with concave bottom, and giving entire satisfaction.

Some English manufacturers do not superheat the steam at all, as they find that in their stills, where it is conducted through the tar in so many fine jets, it is by this alone superheated to the temperature of the tar. I have observed also at a German works, where the steam was simply introduced by a cross of tubes, that no special superheating took place, the superheater formerly employed having been dispensed with. But the steam was previously dried, and caution was always used in first starting it, as any water carried into the still would cause an explosion when suddenly brought into contact with tar possessing a temperature of  $300^{\circ}$  or more. This has actually taken place at several works. For that reason alone we would advise in any case such a slight previous superheating as will *completely* dry the steam, which can be done without any expense whatever.

The employment of dry steam at the end of the process has the further advantage that in running off the pitch no air need be admitted into the still, which otherwise might lead to explosions or fire.

Currie (*Chem. News*, xxxi., p. 175) asserts that the yield of anthracene is increased if a little brimstone is added to the tar, whereby hydrogen sulphide is formed. We do not know whether this proposal has ever been carried out in actual work.

The following statements are made referring to the production of at least 2 tons of oils from crude tar by the application of superheated steam. The apparatus, which requires a ground



space of 16 × 13 sup. ft., and a height of 20 to 23 ft. is supposed to be placed in an already existing building.

For the above-mentioned duty we require *per annum* about 1500 tons crude tar, from which about 300 tons of oils and 900 tons of hard pitch are obtained. Taking the price of tar at 35 marks, and the selling price of pitch at 45 marks per ton, the costs are as follows:—

A. *Cost of plant*—

	Marks.
Apparatus, tubing, reservoirs and pumps, cost of erection, brickwork, etc. . . . .	14,500
Unforeseen expenses . . . . .	500
	<u>15,000</u>

B. *Cost of working*—

	Marks.
Interest on 15,000 M. at 5 per cent. . . . .	750
Wear and tear, at 10 per cent. on 15,000 M. . . . .	1,500
Repairs, at 4 per cent. on 15,000 M. . . . .	600
Tar, 1500 tons at 35 M. . . . .	52,500
Steam, 300 tons at 3 M. . . . .	900
Tar for heating, 30 tons at 35 M. . . . .	1,050
Attendance . . . . .	1,000
Water, Lighting . . . . .	200
Insurance and unforeseen . . . . .	600
	<u>59,100</u>

C. *Value of products*—

	Marks.
Pitch, 900 tons, selling at 45 M. . . . .	40,500
Own costs for 600 tons tar-oil . . . . .	18,600
Own costs for 100 kg. tar-oil at works . . . . .	3.10

Kubierschky's tar-distilling apparatus, according to C. H. Bormann (*J. Gasbeleucht.*, 1914, p. 1037), allows of distilling the tar down to real hard pitch without the application of a vacuum, and in a continuous way, free from any danger. It consists of columns into which the tar is continuously introduced in a thin jet, which is divided into a spray, superheated steam being continuously passed in from below and coming into direct contact with the tar. The steam effects the volatilization even of very high-boiling oils at a comparatively low temperature. The composition of the vapours is depending on the proportion of the vapour tension of the water and that of the oils at the given temperature. The higher the boiling-point of the oil, the more steam is required for driving it over

If, for instance, we distil various oils boiling at  $200^{\circ}$ ,  $300^{\circ}$ , and  $400^{\circ}$ , at  $100^{\circ}$  and atmospheric pressure by means of direct steam, the quantity of steam passing over with the oil vapours rises in the proportion 1 : 8 : 60. This proportion is essentially improved by carrying on the distillation at a higher temperature. If, for instance, we distil at  $200^{\circ}$  by means of superheated steam, the proportion of steam to the oil, other conditions being equal, rises only from 1 : 1.6 : 2.4. In Kubierschky's apparatus the distillation takes place *gradatim* in such manner that the vapours are at once separated from the remaining liquid. Hence no more easily boiling oils get into the bottom chamber, and the residue leaves the apparatus in the shape of liquid hard pitch. This process is applicable to every description of tar, from gas-retorts, gas-producers, coke-ovens, lignite-tar and wood-tar.

By means of superheated steam, it is possible to obtain with this apparatus pitch of medium hardness, or quite hard, in a continuous process.

A special patent of the same inventor provides for an economy of fuel, by cooling down the mixture of oil vapours and steam, leaving the column, only to about  $105^{\circ}$ . Thereby the oils are almost completely condensed, whilst the aqueous vapour remains as steam, and is passed back into the column through a superheater.

This apparatus is built in different sizes, up to a duty of 60 tons tar *per diem*.

There is absolutely no danger of fire, since this is not employed in the apparatus, and only a few litres of tar are heated at the same time. No vacuum is required, and the yield of oils is greater than in the old still process. The quantity of steam required for distilling 100 kg. tar down to hard pitch is only 20 kg., corresponding to about 3 kg. coal. The supply of tar and steam is automatically regulated, so that next to no manual labour is required.

#### *Mechanical Agitators in Tar-stills.*

Sometimes mechanical agitators are employed in tar-stills in order to avoid superheating the bottom at the end of the process. Thus Berninghaus (Ger. P. 4586) provides the still with

a stirring-apparatus like a ship's screw. Lennard (*J. Soc. Chem. Ind.*, 1883, 239) employs a horizontal cylinder, 20 ft. by 7 ft. 6 in., provided with an agitator. Fenner (B. P. 13629, 1884) combines mechanical agitation with the action of steam. Mechanical agitators are also mentioned in Audouin's patent (No. 1456, of 1872), along with agitation by means of a stream of illuminating-gas, carbon dioxide, air, smoke-gases, or steam. It is asserted that in this way 10 to 15 per cent. more anthracene is obtained than usual.

Mechanical agitators are especially found useful when distilling tar very rich in fixed carbon, which sometimes occurs in large quantities, and in the distillation of the tar causes the formation of hard crusts of coke at the bottom of the still. This is prevented either by injecting superheated steam, as before mentioned, or by a mechanical agitator, consisting of a revolving shaft with chains dragging along the bottom. In one trial with this apparatus, after fifteen distillations the still-bottom was found to be almost quite clean, and much less coal had been used for firing. The rivet-heads, as well as the links of the chain, were certainly ground off, and it was found necessary to renew the chain and to re-rivet the still-bottom after six months, but this last drawback could be avoided by countersinking the rivets. There was no deformation of the still-bottom. In this way it became possible to distil such tar down to hard pitch, which was softened again by the addition of dead oil.<sup>1</sup>

It does not seem necessary to employ agitators in the case of ordinary tars. At Beckton, where Fenner's agitators had been introduced in some of the stills, Mr Wilton found no advantage against the system of simply blowing in steam during the latter part of the distillation, and the use of the agitators was therefore discontinued.

Rispler (*loc. cit.*, p. 409) mentions a large tar-works which distilled the tar of the Vienna gas-works, containing a very large proportion of fixed carbon (24 per cent.) in upright retorts, holding 32 tons, provided with agitating-gear for the purpose of avoiding the formation of coke during the distillation. For the same reason the fireplace is not below the still-bottom, but in front of the stills, and the still-bottoms are strongly arched, which causes the coke to slide down to the

<sup>1</sup> *Wagner-Fischer's Jahresber.* for 1885, p. 464.

protected sides, as well as effecting a better penetration of the heat into the centre of the contents. These stills are 13 ft. wide, the sides 10½ ft. high, the top arch 2 ft. 6 in., and the bottom arch 4 ft. high. The mantle is made of six plates, three for the circumference and two for the height. This enables an

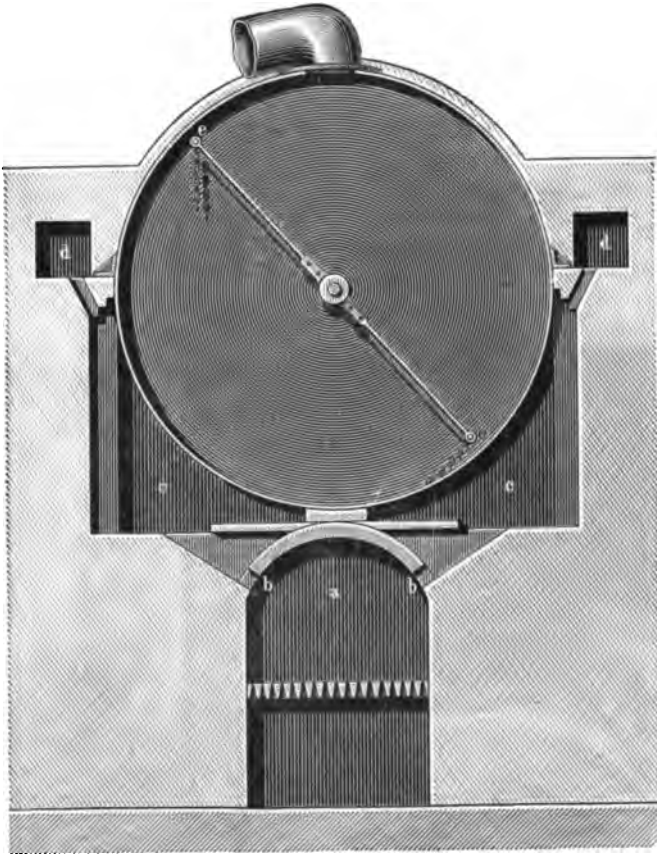


FIG. 109.

easy replacement of the front plate where the flame comes out from below. The bottom plates have a thickness of  $\frac{1}{4}$  in., the lower mantle plates  $\frac{1}{2}$  in., the upper mantle and the top plates  $\frac{3}{8}$  in. The fireplace consists of two compartments, with separate grates, fire-doors, and ash-pit doors.

At some Scotch works mechanical agitation is employed,

not during the distillation itself, but at the end, when heavy oil is run in for the purpose of softening the pitch. This is done at Dalmarnock, Glasgow (Messrs George Millar & Co.). Figs. 109 and 110 show the stills there used, as described in Dr Ballard's *Report to the Local Government Board for 1878 and 1879*, p. 139. Several stills, in the shape of horizontal iron cylinders, 21 ft. long and 8 ft. 6 in. diameter, are placed side by side in a set. The heat from the fire *a* does not impinge directly upon the bottom of the still, the fireplace being arched over along its whole length. The fire-gases pass through twenty openings (*b b*), on each side of the arch into the flue *c c*, and thence through similar openings into the flue *d d*,

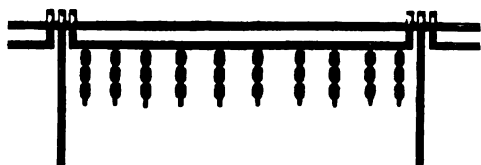


FIG. 110.

leading to the chimney. The still-bottom touches the arch, but does not rest upon it, the still being suspended by stout angle-irons from the side masonry. In order to keep the inside of the still-bottom clean, horizontal bars (*e e*), shown in elevation in Fig. 110, reaching to within 3 in. of the shell of the cylinder, are made to revolve. To these bars are attached, at intervals of a few inches, short pieces of iron chain which drag along the bottom and prevent deposition. The chains are arranged upon the bars so that those of one of the bars scrape the cylinder-bottom in the places in which it is not scraped by those of the other bar. This apparatus lasts for many years without repairs.

Fig. 111 shows the arrangement of stirring-apparatus for an upright still, holding  $7\frac{1}{2}$  tons, and worked with a vacuum. The advantage of all such apparatus is doubtful, and they are only exceptionally employed.

In lieu of mechanical agitating-gear, the stirring-up of the contents of the still may be effected *by blowing in dry steam*, as described on pp. 455 *et seq.*, which both prevents the adhesion of coke to the bottom of the still, and protects the still-bottom against excessive wear and tear by cooling and rapid removing of the tar vapours.

*Distillation in a Current of Inert Gases.*

Craig (B. P. 7615, 1907) distils blast-furnace tar with *an inert gas*, such as blast-furnace gas, producer gas, or flue gas, instead

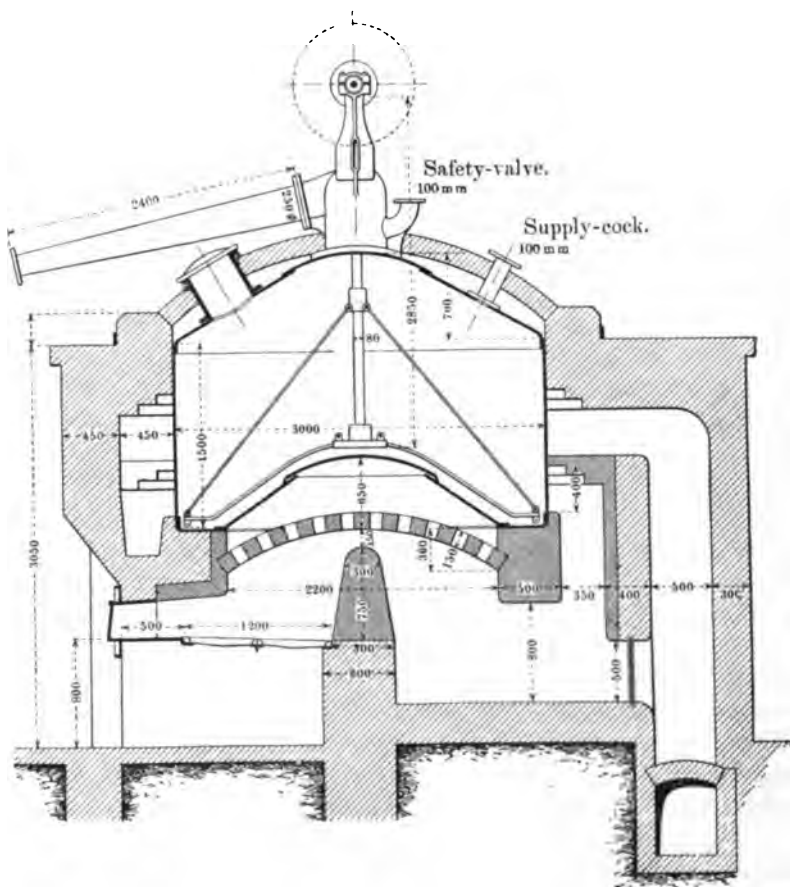


FIG. 111.

of air, in order to prevent oxidation, and to improve the quality of the pitch and oil produced.

A. G. Duncan (U.S. P. 1116578) describes a still, specially intended for this purpose. It is divided into sections by horizontal plates, upon which the liquid is retained by damming walls.

*Application of a Vacuum in the Still.*

The diminution of pressure within the still by means of a vacuum-pump has very great advantages and is more and more coming into use. The author saw it first performed (in 1880) at a German works in the following manner:—The distillation is commenced at the ordinary pressure, and continued till it is time to change for anthracene oil. Now a steam-pump is started, which aspirates both gases and oils away from the condensing-worm into a large boiler sunk in the ground, where the anthracene oil remains whilst the gas is forced out by the pump. From the same pipe steam is injected into the still, as above described, but merely to keep its bottom clear; for no choking-up ever happens, even without the steam: the pump sucks away the butter-like mass quite easily into the boiler. The vacuum-gauge in this showed 15 mm. mercurial pressure. On their passage through this boiler the products were cooled, so that the gas coming out of the far end entered the pump nearly cold. When the distillation was finished, the same boiler served as a pressure-apparatus for forcing the oils into the anthracene-crystallizers. The whole arrangement answered so well that a second apparatus of the same kind had been mounted for creosote oil; but this had not started at the time of the author's visit. The greatest advantage of this plan is the regularity of working, and the complete absence of any danger of choking-up the pipe. An injector had been tried in lieu of the steam-pump, but had not answered so well. The sketch (Fig. 112) may serve for elucidating the process. In this, *a* is the tar-still, *b* the condensing-worm, *c* the anthracene-oil-boiler with its dome, vacuum-gauge, steam-pipe, etc.; *d* the air-pump.

The pressure within the still in this way is usually brought down to about 4 in. of mercury, and the boiling-points are thereby lowered about 80° C., which not merely hastens the process, but is of decided advantage for the quality of some of the products, especially the anthracene.

The first introduction of the vacuum in tar-distilling appears to be due to Mr S. B. Boulton, who applied it in more widely extended ways than that just described, and in such a manner as to prevent all nuisance. The following description of his arrangement is taken from Dr Ballard's Report to the Local

Government Board for 1878 and 1879, p. 142 :—"But the most perfect arrangements for preventing nuisance from uncondensed and non-condensable vapours and gases that I have seen are at Messrs Burt, Boulton, & Haywood's works at Silvertown, near the Victoria Docks. From each condenser the condensed and uncondensed matters pass into a receiver having an opening at the top, which is firmly closed down, during working, with an accurately-faced iron cover. Out of this receiver the condensed liquids are drawn off below to the store-tanks, while the uncondensed gases and vapours are drawn off above by an air-pump or gas-exhauster, worked by a small steam-engine provided for the purpose. These gases and vapours from all the whole row

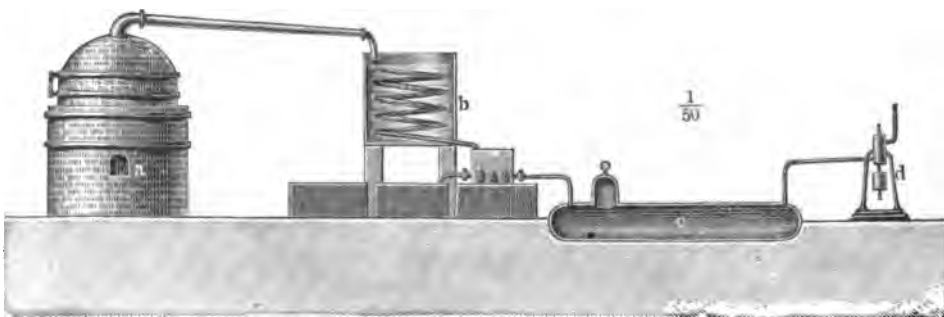


FIG. 112.

of receivers pass into an exhaust-main, which communicates with two 'washers'—the first arranged like a chemist's Woulffe's bottle. They have to pass through both of these, where a certain amount of further condensation takes place. They then pass through the exhauster to a third condenser or 'washer,' shaped like a boiler; and here again they have to pass through water and over water for some feet to the discharge-pipe, which conducts such as are still uncondensed to a fire, where they are consumed. This exhausting arrangement has the further value of assisting to draw off the products of distillation from the still, and to clear this of offensive gases which would otherwise escape into the air during the process of recharging with tar. Another advantage which these manufacturers say they thus obtain is that the watery vapours (containing sulphide of ammonium) which accompany the naphtha and benzol series of products, and which were formerly wasted, are now collected



and utilized for the manufacture of sulphate of ammonia. The benzols also themselves are increased in bulk from the greater care with which these lighter vapours can be collected. Further, by the use of the air-pump and the closed receiver, the duration of the whole distilling operation is abridged very sensibly, which is itself a source of great economy in a large manufactory."

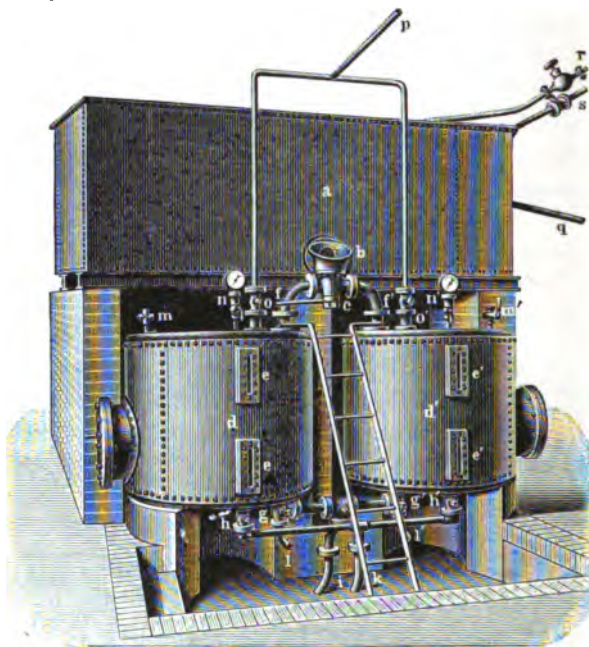


FIG. 113.

A somewhat complicated apparatus for distillation (of alcoholic liquors) in a vacuum has been constructed by N. Galland (Ger. P. 17972, 1881).

Krey has greatly improved the apparatus in such a way that the fractions can be changed without interrupting the vacuum, as shown in Fig. 113. The end of the worm *a* is connected with the cast-iron "pear" *b*, shown here without its cover. The cover is ground on, and is provided with "sights" made of hardened glass. The tree-way cock *c* communicates through *f* and *f'* with the receivers *d* and *d'*. These are provided with glass "sights" (*e* and *e'*), pressed

against the faced edges with asbestos packing on one side, and two indiarubber washers on the other. They are further provided with vacuum-gauges ( $n\ n'$ ), air-cocks ( $m\ m'$ ), blow-off-cocks ( $g\ g', h\ h'$ ), and manholes; with the air-pump they are connected by the cocks  $o\ o'$ , and the branch-pipe  $p$ . We also notice the steam-pipe  $r$ , water-pipe  $s$ , and overflow-pipe  $q$  in the cooler.

During the time the first runnings and light oil are distilling the "pear"  $b$  is covered by an ordinary glass jar. As soon as the creosote-oil period begins the air-pump is started, the receiver is changed, and the pear is closed with its cast-iron cover. The vacuum acts only upon the receiver actually at work, and is cut off from the other receiver by the three-way cock. The previously filled receiver is emptied through one of the cocks  $m\ m'$  or  $g\ g'$  by the pipe  $i'$ , into a store-tank below, the ammoniacal liquor having been first run off through  $l$  or  $l'$ . If the receiver at work is filled, or if the state of the liquid as observed through the "sights" calls for changing the fractions, the empty receiver is connected with the vacuum-pump, and when this has operated sufficiently the three-way cock  $c$  is quickly turned round. The oil contained in the full receiver, when the vacuum-cock has been shut and the air-inlet opened, is run out by  $h\ h'$  and  $i'$  into a pressure vessel below, and forced from this into a collecting-tank. Thus the work is continued until the still is finished.

I am informed by Dr Kraemer that he introduced that system already in 1881 in all the factories belonging to the Aktien-Gesellschaft für Teer- und Erdöl-Destillation, and that they merely applied it to the treatment of browncoal-tar.

Although there is no difficulty in taking samples for testing the distillates during the vacuum distillation, some prefer to work off a still without the vacuum; thereby the bulb of each fraction is fixed, and this serves later on as guidance for the vacuum distillation. During the last period the firing is discontinued, and when all the oil desired has distilled over, the vacuum-pump is turned off and the air is slowly admitted into the still through the receiver.

The quality of the distillates is decidedly improved by the vacuum distillation, and the yield, especially of anthracene, is increased. The objections opposed to this plan by Kissel ( $Z$ .

*angew. Chem.*, 1893, p. 61) are certainly unfounded, especially as most tar-works do *not* employ mechanical agitators for vacuum stills (as he believes to be the case). On the other hand, the principal works employ steam and vacuum combined, as described above.

Weyl (Ger. P. 153222; B. P. 12122, 1904) describes an apparatus, intended for a very high vacuum, consisting of a kind of locomotive boiler, a horizontal cylinder with a fireplace in front and a large number of heating-tubes inside, which are completely surrounded by the tar.

In the case of large, upright stills, the vacuum generally is from 500 to 600 mm., only exceptionally above that.

Steinschneider (Ger. P. 285969) passes the uncondensed gases and vapours before entering the vacuum-pump through a liquid column of changeable height and corresponding boiling-temperature.

The advantage of distilling coal-tar in a vacuum is not merely the saving of time and of fuel, and of reduced wear and tear of the stills, but also, owing to much more perfect fractionation, a superior quality of the distillates and a larger yield, especially of anthracene.

At all tar-works the vacuum is produced by large air-pumps, each of which serves for a number of stills. The application of steam-jet exhausters, as they are usually employed in lignite-tar distilleries, has not been found advantageous for large-sized coal-tar stills, owing to the enormous consumption of steam.

At the end of the distillation the air-pump is disconnected from the stills, and air is allowed to enter slowly through the receiver into the stills.

#### *Running off the Pitch.*

When working in the old manner (*i.e.*, without steam, etc.) it is necessary to fire up to the end, and that sharply. As soon as it is considered that the operation is at an end, the fire-door is opened, the coals are drawn out, and soon the distillation ceases. But the pitch cannot be run off at once, partly because it is too hot (at least 400°, when distilling down to hard pitch), and there is danger of its taking fire, and partly because the large amount of heat stored up in the still and the brickwork might damage

the still. There are also very acrid vapours given off by the hot pitch which are objectionable to the neighbours, although they do not seem to be actually injurious to health, and it is even a fact that children, suffering from skin and lung diseases, are brought to tar-works to inhale those vapours, frequently with a curative effect. Hence some time must elapse before the pitch can be run off with the precautions prescribed above—two, six, or even twelve hours, or even longer, according to the size of the still. After the pitch has been let out, some hours must again elapse before coal-tar is pumped into the hot still, lest the sudden contraction on cooling should start the rivets, etc. At first sight it would seem most suitable to wait rather longer before letting out the pitch, and thus further to diminish the danger of its taking fire; but it is much more important that the pitch should be perfectly liquid when run off, so as to leave the still completely empty. The outlet-cock must be arranged with the same view. Whatever pitch remains in the still is changed by the heat retained by the brickwork into coke, which covers the still-bottom as a non-conducting layer, does not dissolve in the fresh tar, and would soon cause the bottom to be burnt away if it were not from time to time knocked off and cleaned out like boiler-scales. In the case of ordinary English stills this must be done after three or four distillations; but proper placing of the cock, protecting the bottom by a curtain-arch, and twelve hours' rest, will prolong the time to about a month.

The treatment of the stills, as regards running off the pitch, is very much facilitated by the use of steam during the last process, and this is not one of the least reasons for introducing the steam treatment. But the operation is very much simpler if *the pitch is softened in the still* before running off. In this case the distillation is, in the first instance, carried on so far that the residue, if it were run out and allowed to solidify, would yield "hard pitch." This is, however, not done, but creosote oil or the oils draining from anthracene (see Chapter VII.) are pumped back into the still containing the liquid pitch, and thus mixtures are produced of any degree of viscosity, or even liquid at the ordinary temperature, the latter being sold as "prepared tar" or "refined tar." The mixture of the liquid pitch and the oils pumped into it takes place without any special appliance, but it is, of course, promoted by mechanical agitation, for which

purpose the Scotch stills, shown in Figs. 109 and 110 (pp. 461 and 462), have been especially constructed.

Cabot (U.S. P. 184132) proposes promoting the distillation of anthracene by blowing *petroleum* into the mass.

Cyrus M. Warren (Ger. P. 12933, 16th July 1880) proposes distilling tar as usual down to hard pitch, then running into the still whilst hot residues from petroleum-refining, and distilling off once more as much of the oils as corresponds to the weight of the petroleum-residues. From this oil anthracene separates, together with paraffin, which latter is removed by hot-pressing. (It is doubtful whether this plan will furnish easily saleable anthracene; nothing is more dreaded by the manufacturers of alizarin than the presence of paraffin in their anthracene.)

More rational would appear the proposal of Wischin (B. P. 1980, 1880), to add gradually, at the last stage of tar-distillation, heavy coal-tar oil, preferably heated beforehand, whose vapours carry away the anthracene without injuring the quality of the pitch.

In order to remove from tar or pitch those constituents which cause "creeping back," H. W. Robinson (B. P. 4159, of 1913; Fr. P. 468320) adds formaldehyde, or other aldehydes, or substances containing or producing such, before or after the distillation. The best plan is, to make that addition during the distillation of the tar, after driving over the carbolic-acid fraction, before the creosote-oil fraction begins to come over. At the end of the distillation in any case some formaldehyde is to be added to the pitch.

Where the pitch is softened in the stills themselves no choking-up of the outlet-cock or taking fire of the pitch in the air on running off need be feared; and crusts of coke on the still-bottom would probably not appear to any great extent, even if steam were not applied, as is now almost universally done.

An outlet-cock can be dispensed with altogether if the soft pitch, after some cooling, is forced out by means of perfectly dry steam or of a vacuum through an upright pipe coming out of the still-top, and conveying the pitch to some safe place. The outlet-pipe should start from the bottom of the still (which in this case may even be convex), and rise perpendicularly to the highest point, and thence descend in a gentle curve; it must be heated up by steam before the forcing-out begins. There

is in this case no danger of any fire in the pitch-cooler; and the process has answered quite well at several works (*cf.* the sketch, Fig. 84, p. 404). But this plan is suitable only for very soft pitch, and in the cold season it gives so much trouble that it cannot be recommended.

At some Scotch works the soft pitch is pumped out from the top of the still, without any exposure to the air, through a close iron conduit, to the pug-mill, in which it has to be manufactured into "asphalt." If this conduit be sufficiently inclined, no cleansing of it will ever be required.

Running off the *soft* pitch (which is not so very hot, and does not take fire in the air nor choke up the cock) is thus easy enough. But the case is different when *hard* pitch is to be run off. Here not merely must the pitch be allowed to cool down to some extent within the still, but it must first be run into a receptacle protected from the air, in which it must remain till it gives off no more vapour and is no longer liable to take fire in contact with the air. Then it is let off into the open pitch-holes to solidify. In this case the outlet-cock of the tar-still should be provided with a cleaning-flange, and with some contrivance for heating it in order to melt the adhering pitch. This is best done at the end of each operation, before the still is charged again; it is then attended with much less danger than is incurred by deferring the heating till it is time to run off. For this purpose the plan shown in our diagram (Fig. 116, p. 476) can be recommended. The cock is placed in a recess of the still-wall; and at each side of it, separated from it by thin walls, the flues descend: if this should not keep it warm enough, a small fire of wood-shavings can be made round it in the recess; or this is filled with sand, which is heated by a small fire. Sometimes a steam-coil is wound round the cock; but steam-heat is frequently not sufficient for melting hard pitch. In any case the cock must be situated at the opposite side to the fire-door, lest the vapours given off from the running pitch be set on fire.

The outlet-cock is connected by a short descending pipe with an iron or brick spout covered over with an iron plate, for conveying the pitch into a chamber where it is to undergo its first cooling (the pitch-cooler). A spout is preferable to a pipe unless the pitch-cooler is immediately beside the still, because

the pitch readily solidifies in this part of its course, which does less harm when it takes place in a spout than in a pipe. The cover of the spout is spread over with earth to keep off the air and prevent cooling; but, notwithstanding, there is always a coat of solidified pitch in it, which must be hacked out afterwards. If the air is not excluded here, the pitch may easily take fire; and the flame would travel to the pitch-cooler, in which case an explosion would be almost certain to follow. The spout must have sufficient fall and no sharp curves. On account of the danger of fire, some prefer a closed conduit from the still to the pitch-cooler, but this may cause much trouble by the choking-up of the conduit.

In the *pitch-cooler*, *pitch-oven*, or *pitch-house* the pitch must be left long enough (say five or six, or even twelve hours) to cease giving off vapours and to run no risk of taking fire when brought into the open air. This cannot be done without the pitch getting rather tough; hence a good deal of it remains behind in the pitch-cooler, and must be hacked out from time to time. The pitch-cooler is either a brick chamber with brick floor and arched top, or else any sort of iron vessel, for instance an old steam-boiler. A brick pitch-house for two 20-ton stills is about 20 ft. long, 7 ft. wide, and 8 ft. high to the crown of the arch; some are very much larger. Each gable-end is provided with a 3-ft.-square manhole, closed by iron doors luted with clay. At one gable-end the pitch-spout enters; and at the opposite end there is a tap-hole just above the bottom, plugged with clay or with an iron bar, from which open spouts lead to the different pitch-holes.

Iron pitch-chambers are either cylindrical or square; they are more expensive, and suffer more by the hacking out, but cool much quicker than brick chambers. But even in a brick chamber the pitch is cooled long before the chamber is needed for the next charge. Iron coolers, indeed, often act too quickly, and cause the pitch to solidify too early, so that they have been sometimes provided with a fireplace, which, however, may cause coking of the pitch. Where the pitch is softened in the pitch-cooler by adding creosote oil, there is, of course, hardly any trouble with solidifying.

The longer the pitch is left in the cooler, the less nuisance by badly smelling gases is produced; its temperature, on

running out, ought not to exceed about  $120^{\circ}$ , and very little vapour is then given off. There is also this additional advantage, that the oily vapours, which cause the nuisance, are thus re-absorbed in the pitch, and make it softer, which means more valuable. But the longer the pitch remains in the cooler, the stiffer it becomes; if kept too long, the discharge-pipe gets choked, in which case the workman generally clears it with a red-hot iron. This proceeding occasionally gives rise to an explosion, and can be entirely avoided by enclosing the discharge-pipe in a steam-jacket.

The Société Française de Fours à Coke et de Matériel des Mines (Ger. P. appl. 29408, of 1910) cools the pitch within the still by passing steam through it, and thus prevents the giving-off of noxious vapours when running the pitch into the coolers, which is brought about by steam-pressure or by a vacuum.

The pitch-cooler must have a vent in the roof for the escape of gas. This is mostly open to the atmosphere; but it is best to carry it to the chimney-shaft in a slanting tube, so that any condensing liquid may run back; or to make it dip about an inch into a vessel filled with water, similarly to the plan adopted in Paris (see below).

A tap adapted to viscid substances, such as partially cooled pitch, is shown in Fig. 114.

F. Lennard (B. P. 4547, 1883) places within the (iron) pitch-cooler a number of wrought-iron pipes, through which cold tar is pumped so as to cool down the pitch and to obtain a preliminary heating of the tar; or else he effects the same object by different arrangements of the pitch-cooler.



FIG. 114.

Petersen-Kinberg recommends for tar-distilleries manufacturing roofing-felt a pitch-cooler which at the same time serves as montejus. It is boiler-shaped, 5 ft. diameter, 15 ft. long, placed in a somewhat slanting position, with an inlet pipe for compressed air, a pipe in the top provided with the following fittings: a tap, for letting out the air during the filling; an ascending pipe, reaching nearly down to the bottom, for forcing the liquid pitch into the receiver for "prepared tar" (there must be a contrivance for cleaning this pipe when the contents of the boiler have turned too stiff); and a running-off



valve, which the inventor, after working it with full success for a number of years, protected by a German patent. This is shown in Fig. 115. A very slight force, exerted upon the hand-wheel *a*, is multiplied many times by means of the screw *b* and the toothed wheel *c*, so that the valve *d* is forced down upon its seat with sufficient intensity to resist any desired pressure. (This contrivance is sold by C. F. Scheer & Co., Feuerbach, near Stuttgart.)



FIG. 115.

Sometimes no pitch-coolers are provided ; the pitch is then left to cool in the still itself till it can be run straight into the open pitch-holes. This plan is decidedly not advisable for *hard* pitch ; the stills must be allowed to rest much longer, and they must be cleaned out by manual labour after each operation.

Lastly, the *pitch-holes* or *pitch-bays* are situate in front of the pitch-house, and connected with it by brick or stone channels, having a good incline and provided with movable covers. They must have a perfectly level brick floor and 18-in. side-walls ; but otherwise their shape is quite indifferent and may be adapted to local circumstances. They should be of sufficient area to make it unnecessary for the pitch ever to fill them to a greater depth than 12 in. ; preferably only 8 in. There must be at least two pitch-holes, to serve in turn, so that at all times the pitch may completely cool down and solidify in one of them. In the heat of summer this is sometimes promoted by squirting water over them. It is expedient to whitewash the floor with lime every time before using it again, to make it perfectly smooth and to facilitate detaching the pitch. Some tar-distillers use ordinary street dust for this purpose, but this always causes a slight deterioration of the quality of the pitch. Hard pitch becomes so brittle that it is easily hacked up with a pick

in large lumps. The dust unavoidably formed is most irritating to the mucous membranes of the eyes; the men ought therefore to protect their eyes by "goggles" or by crape; and this kind of work is always done by preference at night. In summer it is of course more disagreeable than in winter.

Watson Smith points out that the pitch-holes ought to be laid out so that no pools of rain-water can remain in them: otherwise the pitch may become honeycombed and much less saleable.

In most Continental works the pitch-bays are entirely covered over with boards, or are enclosed in a galvanized iron chamber, provided with movable shutters, to avoid any nuisance.

In very small tar-works there are sometimes no pitch-bays, but the pitch is ladled or pumped out of the cooler into tubs, casks, etc. In this case explosions occur sometimes in running in pitch from the stills, just after a pitch-house has been cleaned from the solidified pitch by hacking it up (Hirsch, *Chem. Zeit.*, 1884, p. 136), evidently because after that operation the pitch-house is filled with fresh air, which sets the pitch-vapours on fire when the contents of the still are running off.

According to Dr Kraemer (priv. comm.), the fires in pitch-houses are generally caused by the fact that the hot pitch chars the wooden parts of the roofs and sets them on fire. He has never observed any explosions. Some ascribe the explosions occurring in pitch-coolers to the fine particles of carbon and pitch floating about in the air; but no doubt these alone would hardly be dangerous without the vapours equally filling the space. Blowing-out the cooler by dry steam after every operation would probably remove all danger from explosions.

Instead of the apparatus just described, a more complete arrangement has been made at the Paris gas-works—an arrangement proposed by Regnault, and which is also found at some large English tar-works. It is represented in Fig. 116. The pitch leaves the still by the cock *a* and a pipe *b* (provided with a cleaning-neck) and runs into the iron box *c*, in which it remains a few hours, till it has cooled down to 200°. From this it goes through the cock *d* and the pipe *e* into a wrought-iron chamber (*f*) half sunk in the ground, 7 ft. wide, 30 ft. long, and 10 ft. deep, which receives the pitch of a number of stills.

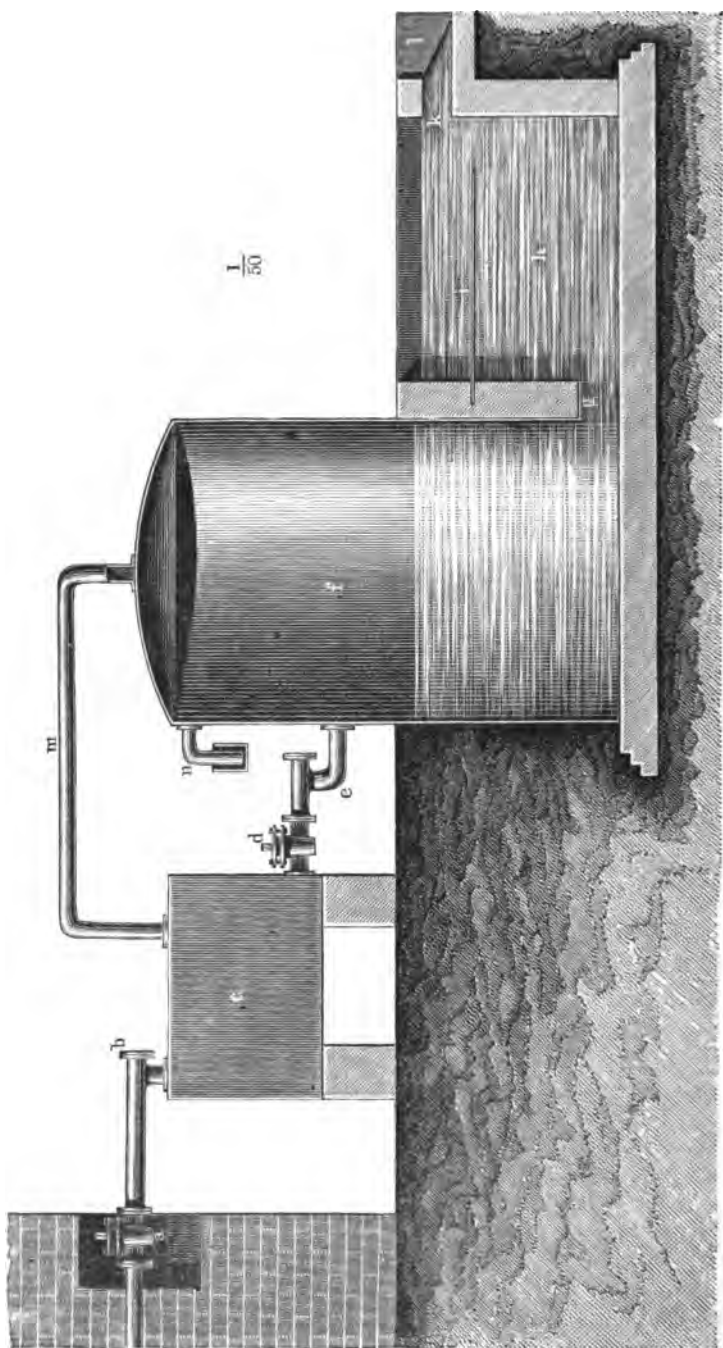


FIG. 116.

Along its whole length runs a brick pit (*h*) 5 ft. deep, communicating with *f* by holes (*g*) near the bottom. An iron plate (*i*) prevents the pitch as it comes from *f*, at a temperature of about  $120^{\circ}$ , from rising at once to the surface; it can only pass along the edge of *i*. The pitch in *f* and *h* remains liquid from one operation to the next, being protected from quick cooling by the subsoil. But on the surface of the pitch above *i* a hard, elastic crust forms; this is promoted, if necessary, by running water over it. Now, if fresh, hot pitch runs out of *a*, it flows in *f* on to the surface of the partly cooled, but still liquid pitch from the last operation; it forces this through *g* into *h*, the still colder contents of which rise past *i* and flow away underneath the crust at *h* into the open pits *l*, where they are left eight or ten days for entire solidification. The very hot pitch in *f* has in the interval time to cool down; the vapours rising from it and in *c*, which communicate by the pipe *m*, are condensed by the surface of iron in contact with the air, and are reabsorbed by the liquid pitch. The pipe *n*, which dips into a vessel filled with tar, allows the air to escape as the tar runs in, and also serves as a kind of safety-valve. But, besides, *f* is provided with a loose manhole-lid, merely luted by Scott's cement, etc., which also performs the office of a safety-valve. This apparatus completely does away with all danger of fire, and with the nuisance arising from the heavy yellow or white, extremely irritating vapour given off by the hot pitch, which will travel as a compact cloud near the surface of the ground to great distances. Whilst observing that pitch was being run off, by the flowing away of tough pitch from the hole *k*, I could not perceive the slightest smell, although standing close by.

These vapours are extremely disagreeable to most persons; but the Government Inspector, Dr Ballard, reports that the only bad effect upon health that he heard of was that they sometimes produce headache, giddiness, faintness, nausea, and perhaps some oppression of the breathing, but never any very serious or permanent ill effects (cf. *supra*, pp. 432 *et seq.*).

The above-described apparatus can be introduced only at very large works where pitch is run off several times a day; otherwise the old charge would stiffen too much before a new charge is run in.

According to Dr Kraemer (priv. comm.), the tap (shown in

Fig. 116 at *d*) is preferably placed in a box, divided into two chambers by a diaphragm reaching not quite to the bottom. The hot pitch runs into the first chamber and forces the partially cooled pitch below the diaphragm into the second chamber, from which it gets into the pitch-cooler. (This is practically done in our figure by the pieces *f*, *g*, *h*, *i*, and *k*.)

At smaller works (distilling not above 10,000 tons tar per annum) it is advisable, in lieu of a pitch-bay, to run the pitch into *moulds* which can be taken to pieces and thus furnish the pitch in loose blocks, without hacking it out. Such moulds can be made cheaply by cutting old tar barrels or petroleum barrels in two, which gives two tubs, from which the pitch can be removed by loosening the hoops and staves. More durable are iron moulds of similar form. They are best placed on a platform, fixed or revolving, and filled from a shoot provided with plugs at suitable distances. Tubs made from old petroleum-barrels (two from each barrel) hold  $1\frac{1}{2}$  cwt. of pitch or a little more; a 15-ton still requires twelve rows of ten tubs each. When containing moisture, they cause the pitch to froth up when run in for the first time, but never afterwards. They need not be painted inside with lime-water or the like; after turning over and loosening the top hoops, the block of pitch comes away by a slight tap with a hammer. To run off the pitch from a 15-ton still occupies two men two hours, and the knocking-out from the tubs takes but little longer. The pitch run into moulds is at once ready for putting on to railway trucks, without any troublesome hacking out, and is quite clean. Both hard and soft pitch can be treated in this way, but in the hot season the knocking-out must be done in the early morning hours. The worn-out tubs are used for firing-up, which is just the fate the old barrels would have suffered in any case.

Iron moulds are made in two pieces, connected by hinges, with a loose bottom. These must be painted inside with lime-water, or a suspension of clay in water, or, best of all, with cheap paraffin oil or some other oil which does not dissolve pitch.

A table in the Alkali Report, No. 30 (1893), pp. 22-29, gives the following data for all English tar-works:—Number of stills, size of the same (from 2 to 40 tons, mostly 10 to 12 tons), description of pitch-cooler, in a few cases the temperature at

which the pitch is run off from the still into the cooler (between  $100^{\circ}$  and  $280^{\circ}$  C.) and from the cooler into the open bays (between almost the ordinary temperature [?] and  $243^{\circ}$  C.), and the means employed for removing the noxious vapours and those for producing the necessary draught.

Bueb (priv. comm.) has constructed an apparatus which is easily attended to by a single man. The pitch, partially cooled but still pretty liquid, is run from the pitch cooler (an old steam-boiler) at first into a small reservoir, standing on a turn-table and connected with a long, open spout which runs on two small iron bogies on semicircular rails. The spout has, in certain distances, arranged according to the diameter of the pitch-moulds, holes of about 2 in. width, stopped by wooden plugs. The pitch-moulds are radially placed underneath that spout, and can be successfully filled by taking out the wooden plugs.

H. Köhler has introduced a similar apparatus which occupies less space. Along the old steam-boiler serving as pitch cooler an iron spout is placed, possessing at the bottom, in distances of 3 in., openings 2 in. wide, stopped by wooden plugs. At a right angle to this spout, and running by rollers on three rows of rails, there is a second spout, similar to the first, below which the pitch-moulds are placed *seriatim*. The work is performed in this way:—At first the running-off spout is put underneath the most outward hole of the fixed spout, and the required moulds are placed below. When these are filled, the spout is moved on up to the next hole, and so on, until all the rows are filled. The moulds may be made of old petroleum barrels which have served for the carriage of tar, but are no more serviceable.

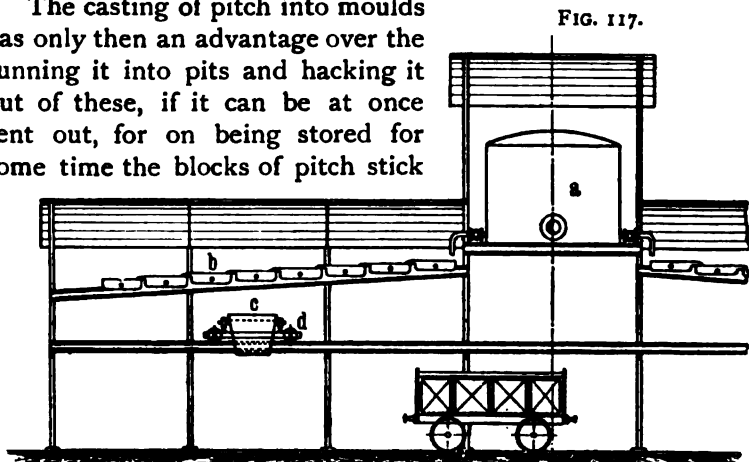
The troublesome formation of dust, which takes place on cutting the pitch out of the pitch-holes, is thus almost entirely avoided. For getting it out of the moulds, it is indifferent whether hard pitch or soft pitch has been obtained; but this should be done during the summer season in the early hours of the day.

At large tar-works the pitch is forced from the coolers into elevated intermediate vessels, from which it is run by spouts into large moulds consisting of two halves; the blocks of pitch coming out of these are directly loaded in railroad cars. Rispler (*loc. cit.*) states that such blocks weigh about 5 cwt. each,

and six hundred of such moulds are required for an annular production of 10,000 tons of pitch.

The pitch vapours are very irritant for the throat, the lungs, and the eyes, and cause more injury to the health of the workmen than pitch dust, which acts merely on the eyes.

The casting of pitch into moulds has only then an advantage over the running it into pits and hacking it out of these, if it can be at once sent out, for on being stored for some time the blocks of pitch stick



to each other, and they must ultimately be hacked up again.

In lieu of the cast-iron moulds composed of two pieces, which have a considerable weight, and in which the pitch, owing to the thickness of the metal, takes a long time to cool down, it is advantageous to employ "spring-moulds," consisting of a single piece of elastic steel-plate, kept together at the joint by two angle irons, by means of cones. When the cones are knocked out, the mould opens of its own accord, and the pitch block comes out without application of force.

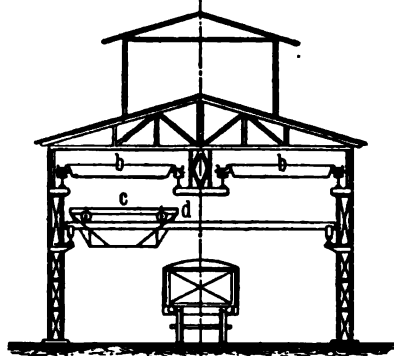


FIG. 118.

An arrangement for running off, cooling, breaking up, and loading the pitch with a minimum of manual labour is described in the German patent of the Chemische Fabrik Lindenhof,

C. Weyl & Co., 217427, as sketched in Figs. 117 and 118. The pitch is forced from the receiver (which is constructed so as to act as a montejus) into the elevated tank *a*, the contents of which are run into the pans *b*, placed in a descending row. The number and size of these pans depends upon the capacity of the tank *a*, and the time required for completely emptying it. By regulating the temperature of the pitch before running it off, it is easy to manage with a given number of pans, at any outside temperature, so as to prevent the pitch from solidifying too soon, and not to get down to the lowermost pan. When this pan is full, the running off is stopped, and when the pitch has solidified in all the pans *a*, these pans, which rest on horizontal pivots, are tipped into the vessel *c*, which is provided with a grate and runs on rails, and is moved on to a railroad car, into which its contents are discharged by opening the bottom. One elevated reservoir *a* may serve for several rows of pans *b*. Only one man is required for serving two rows of pans.

Graf (Ger. P. 224257) cools the pitch by water, which certainly requires a more complicated apparatus than the cooling by air.

#### *Continuous Distillation of Tar.*

Frequent attempts have been made to render the distillation of tar a continuous operation, involving a constant inflow of fresh tar and outflow of pitch.

Mallet<sup>1</sup> causes the tar to circulate on a sufficiently long lead bath, where it successively gives off light and heavy oils, and at the end runs off as pitch. The fractionating is effected by making the tar pass round divisions which do not impede its circulation, but separate the vapours into two or three classes. According to Knab, nothing is gained by this plan.

A proposal made by Vohl<sup>2</sup> is likewise intended to carry out a fractional distillation at a constant level, especially in order to meet the disadvantage of the light oils being kept back by the heavy oils. This is effected by the apparatus delineated in Fig. 119. A and B are cast-iron stills; C, a feed-pipe dipping 3 or 4 in. into the liquid; D D,

<sup>1</sup> Girard and Delaire, *Derivés*, p. 11.

<sup>2</sup> *Dingl. polyt. J.*, clxxvii., p. 133.



manhole-lids; E, pipe for conveying the vapours given off in A to B; F, pipe for the vapours going from B to the separator G; H, pipe for the heavy oils, connected with a refrigerator; I, pipe for the light oils, also connected with a worm; K, connecting-pipe between the two boilers, with the stopcock U, to be opened and shut by the handle L, in order to let the liquid flow from B into A. *m* and *n* are floats; *m* is so arranged that, on the liquid in A rising above the level *a*, the float shuts the supply-cock of C; *n* is connected with a loose

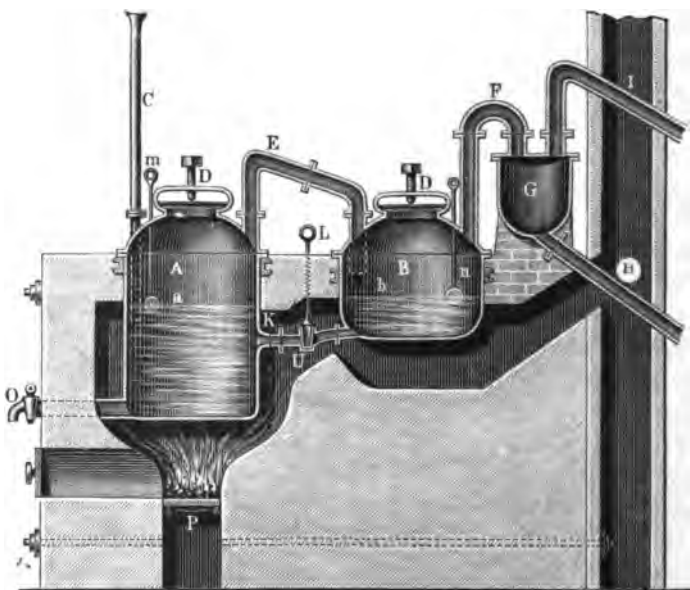


FIG. 119.

valve which opens whenever the level rises too high. O, outlet-cock for the heavy oil residue in A; P, fireplace; V, stoking-hole. To start the apparatus, A is filled through C up to the level *a*, its contents heated to boiling, and then a continuous supply run in through C. Until the ebullition in A is very strong, the flame is kept off B by a damper, and is directed straight to the chimney.

Meanwhile B and G are getting heated, and from H a constant stream of oil distils off. Now by opening the damper the fire from P is directed underneath B; and from this time

light oils distil from I, heavy oils from H; the heaviest oils remain behind in B. If *m* shuts off the supply-cock, the fire must be increased. Also, if the valve *n* in B is lifted, this is a sign of too little firing, too much being condensed in B; or else the damper keeping off the fire from B has been raised too late. When A has been worked off, which is soon known by experience, the fire is damped by wet ashes and the residue from A let off through a refrigerator (consisting of a set of cast-iron pipes immersed in water) into a tightly covered iron vessel. Then the contents of B are run through U and K into A, the level is made up to *a* by supplying tar through C, the damper for B is let down, and the operation is recommenced. Such an apparatus (erected by Thiriart & Co., of Cologne) is said to yield  $1\frac{1}{2}$  ton of light oils in twelve hours. It was originally intended for paraffin oils; but Vohl believed that it is also eminently suitable for coal-tar, and would yield twice the usual quantity of benzene and its homologues.

N. M. Henderson (B. P. 540, 1883) has constructed a similar apparatus, consisting of three horizontal cylinders, about 7 ft. diameter and 9 ft. long.

We pass over the patents of Ellison and Davis (B. P. 13929, of 1886) and of Max Böhm & Co. (Ger. P. 60747), to give a description of Lennard's continuous still (B. P. 7334, 1888), shown in Figs. 120 and 121. The still (C), divided into compartments (*cc*), partially dips into the oil-bath B. The compartments are arranged in steps, with inclined bottoms and with inlets and outlets at opposite sides, to force the tar to travel by the longest possible route. D is a steam-pipe, with branches (*d*) for each compartment, ending in perforated pipes. The compartments nearest to the tar-inlet pipe A have recesses (E) in their bottoms, with partitions (*e*). On one side of these the steam-pipe *d* and its dividing-pipes (*b*) are introduced. The tar enters at A, fills the recesses E, passes on the opposite side into the second compartment, and so on, being gradually distilled by the heat of the oil-bath and the steam until it has been converted into pitch, which runs out continuously at F. The tar, before entering the still, is heated up to the boiling-point by a spiral (Y), lying in an oil-bath (B), afterwards in a scrubber by steam passed through the opposite way. The vapours produced are condensed in some apparatus, cooled

either by tar itself or by products distilled from it, which by this operation are redistilled and thus rectified.

According to a later patent of Lennard's (B. P. 844, 1891), the tar, previously heated by being used as a cooling-agent, is superheated in closed coils of pipes, and on entering into a scrubber is freed from volatile matters by a current of steam,

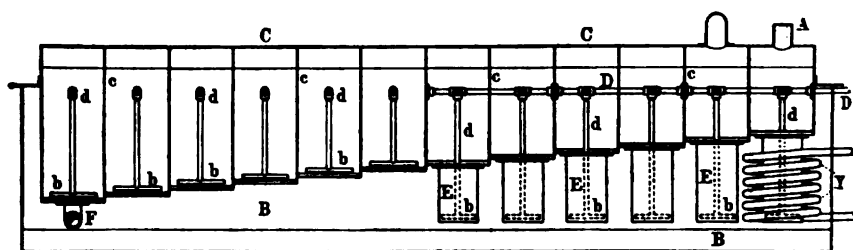


FIG. 120.

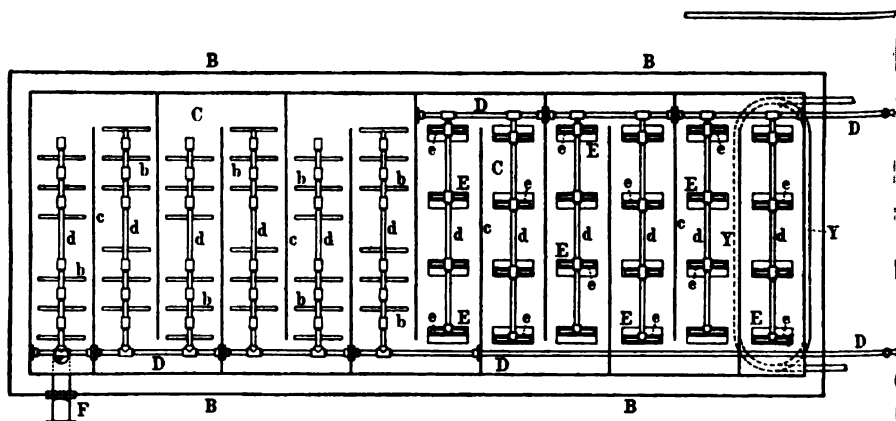


FIG. 121.

the pitch flowing away into a cooling-chamber and at last into pitch-bays. The superheating is done in sand-baths, fitted with iron worms.

The *Alkali Report* for 1894, p. 126, states that no noxious vapours are given out by this apparatus, but on the economical success of the plan no certain opinion could be given. In 1895 there were two such stills at work at Messrs Forbes, Abbott, & Lennard's, at East Greenwich, one for 16,000, the other for

24,000 gall. of tar in twenty-four hours; also one in Scotland and another on the Continent.

Later on this system seems to have come more into use. Löw-Beer<sup>1</sup> reports very favourably on the Lennard stills in their improved shape (Fig. 122). The raw tar, after being freed from coarser impurities by a sieve, is pumped by pump B, and is first employed as a cooling liquid in the creosote-oil condenser H and in the anthracene-oil condenser J, and during this function it is already deprived of the ammonia water and

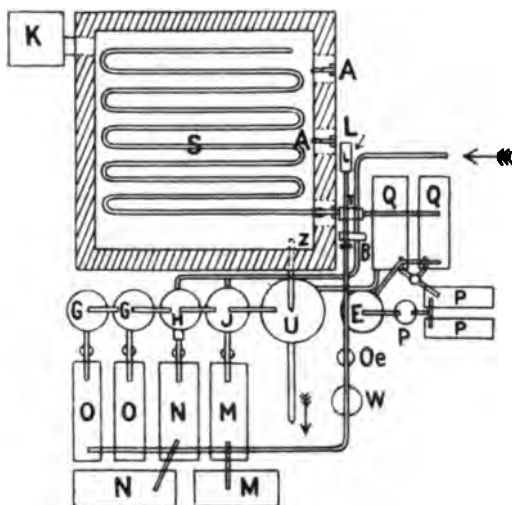


FIG. 122.

of the lightest oils. It then passes through a "tar-scrubber" (E), consisting of a column filled with fireclay rings, and provided with an arrangement for heating it by means of superheated steam (which is merely used in the commencement, before the raw tar has had an opportunity of taking up heat in the oil-condensers, as described above). In the scrubber E the removal of the water and the lightest oils goes on, and is continued in a condenser (F), before the tar gets to the reservoirs, P P and Q Q. From these, still in a warm state, the tar is forced by a pump (T) into the distilling-apparatus S. This consists of two cast-iron coils, one above the other, placed in a heating-furnace. The fall in these coils is quite regular, and amounts to 18 in.

<sup>1</sup> *Z. angew. Chem.*, 1905, p. 8.

in all. The diameter of this pipe increases towards the hotter, lower part, corresponding to the expansion of the tar by the heat, the difference of diameter between the beginning and the end of the coil being 2 in. On leaving this distilling-coil at *s*, the tar has a temperature of 300°. It now runs into the "pitch-scrubber" U, where it flows over large surfaces, and is heated by a current of superheated steam to about 300°; here it yields the remainder of the volatile substances and leaves the scrubber in the shape of hard pitch, or, if desired, of intermediate qualities, as regulated by the temperature of the steam.

The vapours driven out by the steam get into a condenser (H), where the anthracene oil liquefies, and collect in N; they then pass the creosote-oil condenser J and the reservoir M, both of which, as before mentioned, are cooled by raw tar; this cooling can be regulated with such ease that the specific gravity of the condensed products does not vary during a number of months. The light oils leaving the condenser H are condensed further on by ordinary water-cooled coils in G G and collected in tanks O O.

The whole system, including the tanks for collecting the various distillates, stands under a vacuum of about 550 mm. (say 21 in.). To prevent losses of ammonia and light oils, a water-tower (W) and an oil-tower (Oe) are placed between the tanks and the vacuum-pump L. There are also samplers, consisting of automatic siphons which act without destroying the vacuum.

The heating of the distilling-coil cannot be done by coal, as this would act too unevenly; it is done either by oil-burners or by gaseous fuel. The fire-gases first heat the lowest part of the coil, where the tar leaves it and gradually gets to the higher part; after this they serve for superheating the steam, and at last escape through the chimney K.

After starting the apparatus, it takes from ten to eighteen hours before hard pitch is formed; during this time the partially distilled tar is taken back into the hot-tar tank by a pipe.

Only one man is required for working this apparatus, but he must know it thoroughly, since awkward accidents may occur through leakages of the coil, etc. These can be observed by a number of "sights" in the furnace, and they would also betray themselves by the thick smoke of burning tar escaping out of

the chimney. As soon as this happens, the attendant must at once stop the firing, as well as the tar-pump, and inject superheated steam into the coil by a tap provided for this purpose, which forces the tar out of it in a few minutes; after this the other parts of the apparatus can be stopped, all of this in a very short time. The man must also constantly look after the pressure-gauges, fixed in various places, which indicate any plugging-up of the pipes. This happens very rarely, as the vacuum prevents it. One such still was nine months continually at work, without a day's interruption.

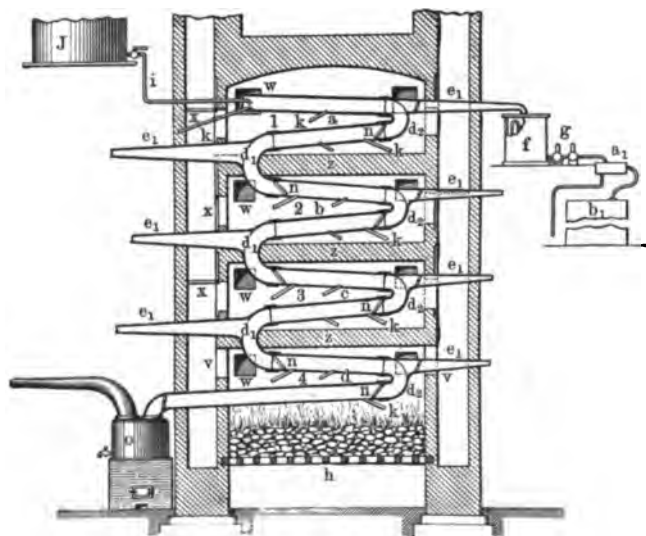


FIG. 123.

One of the stills at the inventor's works can work off up to 150 tons of tar in one day. Almost the only drawback of the system is that the cost of it is high, and does not pay when less than 5000 tons of tar per annum is consumed.

Mason's continuous still (Ger. P. 66097) is primarily intended for petroleum, but is equally applicable to coal-tar. The retort (Figs. 123 and 124) is formed of zigzag pipes, and is composed of as many single chambers (*a, b, c, d*) as there are distillates to separate, or else of one continuous tract (Fig. 124). The single parts are arranged one over another in a special space of the furnace (1, 2, 3, 4), divided by partitions (*z*) or flues. *e*<sub>1</sub> are

still-heads, issuing from the bends  $d_2$ ,  $f$  coolers,  $a$  receivers,  $g$  a vacuum-pump,  $b$  reservoirs for the products,  $h$  fireplace,  $k_1$  steam-jacket,  $k_2$  regulating sand-bath. Every chamber can be heated separately, or cooled by flues ( $w$ ) in a methodical way. The oil or tar, contained in  $J$ , is introduced through  $i$  at  $a$ ; a steam-jet ( $k$ ) converts it into a spray, which is repeated in every compart-

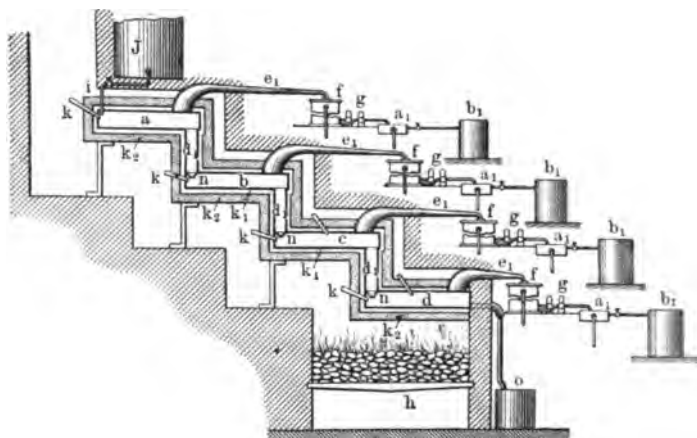


FIG. 124.

ment, the sprayed oil being driven along the hot retort-sides and the last residue is run into  $o$ .

Pfropfe's still (Ger. P. 55025, 1890) consists of a semi-cylindrical trough (Figs. 125 and 126), divided by partitions ( $S$ ) into compartments ( $A$ ), with communications at  $s$ .  $T$ , inlet for the tar;  $H$ , still-heads for every compartment. The pitch runs through  $s$ , back through the still, and there gives up most of its heat, till it issues at  $h$ . H. Köhler had the opportunity of working such a still during four months. It had a diameter of 3 ft. 3 in. and a length of 14 ft., and consisted of eight compartments, each provided with a still-head and cooler. It distilled 3 cwt. of tar per hour, with a consumption of 10 per cent. good coal. Dry steam was blown into the heavy-oil compartments to prevent the formation of coke. The distillation of the first runnings and of light oil was easy, less so the separation of carbolic oil from creosote oil, but that of the anthracene oil was again better. The pitch-pipe  $s$  was frequently obstructed, and was therefore superseded by running the pitch from the

last compartment directly into a closed cooler. The distillation could not be easily carried on in such a manner that the products



FIG. 125.



FIG. 126.

were always of even quality, and this would have to be improved by a regulated system of firing. The following curves (Fig. 127) allow a comparison between the results of a Ppropfe still

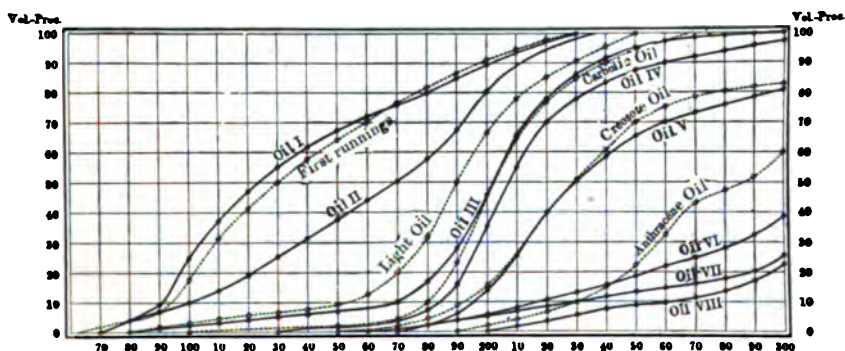


FIG. 127.

(dotted line) and those of an ordinary upright vacuum-still (continuous line), which proves that the former are equal to the latter.



There is a certain saving of fuel and of labour. In its improved shape Pfropfe's still is best adapted for removing only the water and the more volatile substances, leaving a material well adapted for the manufacture of roofing-felt (p. 353).

The continuous still made by H. Hirzel at Leipzig-Plagwitz (Fig. 128) admits of employing surprisingly low temperatures

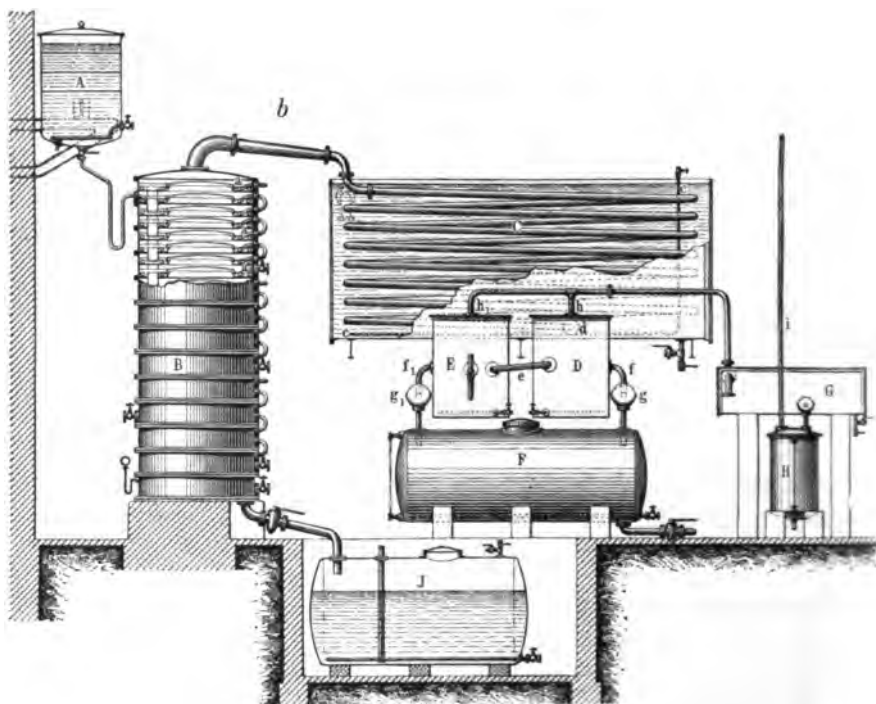


FIG. 128.

for distillation. Instead of working up to  $300^{\circ}\text{C}$ .,  $150^{\circ}$  or  $160^{\circ}\text{C}$ . is sufficient, or for anthracene oil and hard pitch  $250^{\circ}$  instead of  $400^{\circ}$  and upwards. Thus very pure anthracene is obtained, and the phenols are recoverable most easily in a pure state. The tar is heated up in A, purified from coarse matters by a sieve, and run through a column (B). At the bottom of every one of the chambers of this column there is a steam-coil (*a*), which, when supplied with steam at 90 to 100 lb. pressure, heats the tar to  $155^{\circ}$  or  $160^{\circ}\text{C}$ . Open steam passes from below to the top and carries off the volatile matters to such a point that at

the bottom only soft pitch issues, containing the elements of hard pitch and anthracene oil. The vapours escape through *b* into a cooling-worm (C); at *d* the condensed oils and water run into the separator D, where the heavy oils sink to the bottom; the water and the light oils pass through *e* into a second separator (E), where the water runs off sideways. The tar-oils from D and E run through *f f*<sub>1</sub> and *g g*<sub>1</sub> into the reservoir F. The contents of the separators D and E are generally warmed up to prevent obstructions by naphthalene, and are therefore provided with pipes (*h h*<sub>1</sub>) leading the benzol vapours into a supplementary cooler (G) and the receiver H. The soft pitch is collected in the steam-heated pressure-tank J. By working the column at lower temperatures it is possible to get at the bottom, instead of soft pitch, a liquid tar, suitable for the manufacture of roofing-felt and as "prepared tar."

The distillate obtained by the usual way of working contains all the oils boiling up to 300°, all the anthracene remaining in the soft pitch. It can be worked up in the usual manner, but Hirzel recommends the following method:—Cooling down by artificial cold and mechanical agitation, separating the crystallizing naphthalene by a hydraulic press, treating the filtered oil with caustic-soda solution, rectifying the remaining oil by steam, and purifying the distillates by sulphuric acid.

The soft pitch can be worked up as follows:—It is forced from J into a higher-placed reservoir and continuously run into a still heated to 250°, steam superheated to the same temperature being blown in, until the anthracene oil has been driven over; the hard pitch is run off from time to time without any danger or evolution of noxious vapours.

Dr Hirzel's process has been practically introduced. It is decidedly less dangerous and causes less nuisance than the ordinary stills, but the apparatus is more expensive and requires more supervision. In 1905 Hirzel obtained a new patent (Ger. P. 172224).

A continuous tar-distilling apparatus, constructed by Walter Köhn, of Lübeck, has roused much attention. It is supplied by the Lübecker Apparatebau-Gesellschaft, of Lübeck, from which I have received the following communications thereon, with permission to publish them, as well as the diagram, Fig. 129.

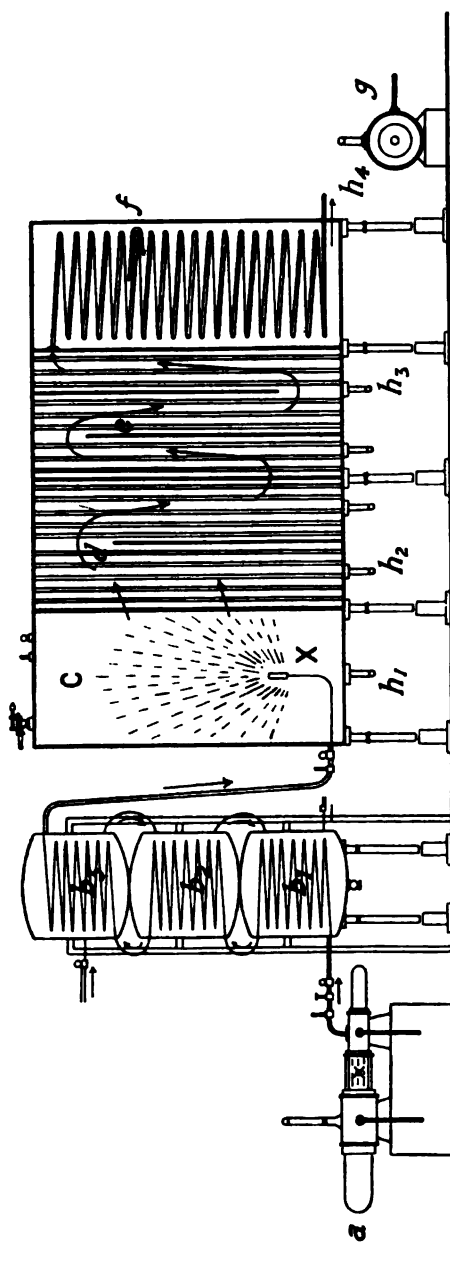


FIG. 129.

The tar is forced by a pump (*a*) through a series of spiral tubes (*b*<sub>1</sub> *b*<sub>2</sub> *b*<sub>3</sub>), heated by a fire or superheated steam, of an aggregate length of several hundred metres. Here the necessary temperature is reached, the velocity of the current of tar being about two metres per second, but the high pressure prevents the formation of gases within the tubes. The heated oil is conducted into the still *c*, where it is throttled by cap *x*, so that it remains under high pressure in the tubes, but on issuing at the cap *x*, which is perforated by many small holes, it is thrown against a baffle plate and is at once converted into a spray, consisting of a mixture of steam and tar-oils, which go on to the coolers *d*, *e*, *f*, whilst the dead oil or pitch runs off at the bottom at *h* into a tank or an ordinary still, to be further distilled. The carrying over of liquid pitch

into *d* is prevented by a series of slanting plates. In consequence of the high pressure no coke is formed in the tubes. Where several apparatus are working alongside, the hot pitch may be used for heating the tubes *b*<sub>1</sub>, *b*<sub>2</sub>, *b*<sub>3</sub>. These are kept at different temperatures, so that *b*<sub>1</sub> gives creosote oil, *b*<sub>2</sub> light oil, and *b*<sub>3</sub> crude benzol, which goes on for months without any fluctuations of the specific gravities. The cooling may be effected by tar, which is thus pre-heated. A 10-ton still can be filled with dehydrated tar within an hour, but it is best to calculate upon two or three hours. One apparatus is sufficient to supply five stills at 10 tons each, one after the other. The tubes *b*<sub>1</sub>, *b*<sub>2</sub>, *b*<sub>3</sub> stand a pressure of 250 atmospheres, but are worked only at about 20 atmospheres. There is no danger of fire, even where the heating takes place by coal, as the contents of the tubes are minimal (there is never more than 150 litres of tar in the apparatus), and by the simple turning of a valve the supply of tar is instantaneously stopped. The liquid cannot boil over, as only very small quantities of it are injected per second into *c*. The work is very cleanly and requires no continuous attendance. This system is employed for various purposes; viz., for merely dehydrating tar, for driving out only the lightest oils in order to get as far as "asphalt" (p. 451), soft pitch or even hard pitch, and quite a number of such apparatus are already at work.

Ray, of Turin, in a communication made to the Chemists' Congress at Rome in 1906, describes a continuously working apparatus for distilling tar (patented in Germany as No. 157502; Fr. P. 348267), consisting of a battery of horizontal iron retorts, inclined in opposite directions, as they follow one another. The ends of the retorts pass outwards through the brickwork, and communicate by means of pipes. Thus a zigzag is formed, into which the tar enters at one end and the pitch flows out at the other. Every retort is provided with an inlet and outlet valve and a pipe for carrying off the vapours. The heating-gas passes first under the last retort and gradually proceeds to the first. The last retort is provided with an inlet for steam, superheated to 250° to 270° C., which facilitates both the escape of the heaviest vapours and the running out of the pitch at a moderate heat, and prevents the formation of coke. It is not necessary to dehydrate the tar before introducing it.

Wilton (B. P. 25879, 1907) employs for distilling tar in a continuous process two retorts, superposed over one another, and inclined in opposite directions, so that the liquid, entering at the top of the upper retort, leaves the lower cylinder at its lower end. Both retorts are combined with tubular coolers. The tar enters at the bottom of the top cooler, leaves it at the top, enters the bottom of the lower cooler, and leaves this again at the top. In flowing through these two coolers the tar is heated up by the vapours from the top retort, through which it afterwards flows in a thin stream, enters the bottom retorts and flows out at its lower end, the surface being increased by a number of projections attached to the bottom of the retorts. After leaving the bottom retort, the liquid residue flows through the bottom cooler.

Kubierschky (*Chem. Zeit.*, 1915, pp. 387 and 422) effects the continuous distillation of tar in a column-apparatus by means of superheated steam, which allows of proceeding at will either up to hard pitch or to middle-hard pitch. The superheating of the steam is effected by an apparatus placed outside the distilling-shed, and is performed by means of oil-residues, tar or a similar kind of fuel. The steam continuously circulates between the superheater and the tar-still. Apparatus of this kind are built up to a duty of 60 tons tar per diem. By this process, in which only a few litres of tar are getting heated at a time, crude, water-containing tar can be distilled without any danger up to perfectly brittle hard pitch in a continuous manner, with separation of the single fractions.

Archdale (B. P. 16511, 1902) employs for continuous distillation a steam-boiler-like box, heated outside, with baffle plates on the bottom, forming a zigzag channel, through which the tar flows in at one end and out at the other.

Other patents for continuously acting tar-stills are:—

Werner & Pfeiderer, Ger. P. 106713.

Bockelberg & Sachse, Ger. P. 154755; B. P. 7204, 1904.

Tack, Belg. P. 181041.

Wilke & Co., Ger. P. appl. D16094.

Artmann (Ger. P. 233233, 1910).

Reichmann (Ger. P. 221898, 1907).

Wernecke (Ger. P. 201372).

Schliemann (Ger. P. appl. Sch. 34048, 1910).

Raschig (B. P. 14230, 1913; U.S. P. 1141265; Ger. P. 260060).

Franz Wolf (Ger. P. 228208).

A. von Gröling (Fr. P. 322789).

Meikle (B. P. 2105, 1901).

Barbet (Fr. P. 398625).

Ilges (B. P. 3302, 1909).

Beck (Ger. P. appl. B58512).

Victor Sadewasser & Co. (Ger. P. 238013; described in detail by Lemmert in *J. Gasbeleucht.*, 1912, p. 321).

The opinions of experts on the practical value of a continuous distillation of coal-tar differ. The majority hold that this system in the present case, where it is not merely a question of distilling in the ordinary way, but of effecting at the same time a separation of the fractions, is not the best for coal-tar, but should be resorted to only in such cases where the masses to be worked up cannot be managed in the ordinary way, *e.g.*, in the case of petroleum oils. But this case may easily set in also with coal-tar, looking at the enormously increasing production of tar in coke-making.

*Distillation of Tar for the Purpose of making Illuminating-Gas.*

The low prices prevailing for coal-tar products during a number of years have led to a proposal to distil the tar in such a way that only those substances are removed which are injurious to the object in question, while all the others, including benzol, are converted into a rich gas. Davis<sup>1</sup> states that gas-tar oils, as well as petroleum spirits and petroleum residues, become gasified whilst passing over red-hot surfaces, and that about 50 cub. ft. of 50-candle gas are obtained thereby from 1 gall., possessing a sp. gr. of 0.912. Taking the oils as weighing 10.8 lb. per gallon, 1 ton would yield 16,600 cub. ft. of 50-candle gas, approaching very nearly to the composition of rich cannel-gas. In order to carry out this process of enrichment on a practical scale (say, for works carbonizing 50 tons of coal per day), a set of three 10-ton tar-stills would have to be provided, so that they might be worked consecutively, one always being run off and refilled. The raw tar

<sup>1</sup> *J. Soc. Chem. Ind.*, 1886, p. 6.

is distilled in the usual manner and the distillate conveyed into three separate tanks, A, B, and C, the still being stopped when a sample of the pitch, on being withdrawn, twists easily at a temperature of  $55^{\circ}$  C., which signifies that it is of very good quality and readily saleable (*cf.* Chapter VI.). The contents of tank A will remain liquid; those of tank B will, on cooling, separate naphthalene, and those of tank C crude anthracene. If tank B is constructed in the form of a filter, the naphthalene can be easily removed, and either worked up, sold, or used as fuel. The oils of tank C must be filter-pressed to recover the anthracene, after which the contents of all are ready to be made into gas. When sufficient oils have accumulated, another still is filled with a mixture from the tanks A and B, and this is slowly distilled, the vapours being passed directly into one end of a through-retort heated to dull redness; the gasified hydrocarbons passing out at the other end by means of the ascension-pipe are mixed with the gas from the ordinary retorts. When four-fifths of the contents of the still have been vaporized, the fire is withdrawn and the still filled up with raw tar, which is distilled as before, and the pitch run out for sale; after which the still is again ready for vaporizing another batch of oils. When sufficient oil from the anthracene has accumulated, it is distilled in whichever still happens to be at liberty. The first fourth is run into the creosote or B tank, the second fourth into the anthracene or C tank, the still being stopped when the pitch will just soften at  $50^{\circ}$ , when it is run off into the pitch-house in the same manner as when dealing with ordinary tar. In this way any gas-works would be able to supply an illuminating gas of good quality without the aid of cannel-coal, and to produce pitch and anthracene of the very best quality.

The calculation would run as follows:—

100 tons of ordinary coal give each 10,000 cub. ft. of gas of 17 candles.

5 tons of cannel-coal give each 12,000 cub. ft. of gas of 28 candles.

Coal produce  $1000 \times 17$  candles. . 17,000.

Cannel „  $60 \times 28$  „ . 1,680.

In all, 1060 cub. ft. at 17.6 candles.

Taking coal and gas-tar:—

100 tons of coal give 10,000 ft. of 17-candle gas.

2.8 „ tar-oils give 16,000 ft. of 50-candle gas.

Coal produce  $1000 \times 17$  candles = 17,000.

Tar-oils „  $46.5 \times 50$  candles = 2,325.

In all, 1046.5 cub. ft. at 18.4 candles.

Davis thus makes out that the 7 tons of tar produced from 100 tons of coal [this is much in excess of the average!] has a value to the gas-maker equal to nearly 10 tons of cannel-coal. One through-retort will give about 500 cub. ft. of gas per hour, equal to the decomposition of some 7 gall. of oil per hour.

Davis's statements are altogether contradicted by Lewis T. Wright.<sup>1</sup> He shows that very little is to be gained by incorporating all the benzene of coal-tar with the gas. Taking the percentage by weight of benzol in coal-tar = 0.8, the percentage of tar on the coal as 6.6, and the quantity of gas to be carburetted per ton of coals as 10,000 cub. ft., we have as the total quantity of coal-tar benzol available per 10,000 cub. ft., 0.1183 lb. Since it takes 1.9 lb. of benzol to bring 16-candle gas up to 17 candles, the above quantity of benzol amounts only to an enrichment of 0.06 candle, which is evidently unremunerative. Neither does the dry distillation of tar-oils lead to the solution of the problem. Wright made many experiments, injecting the oils into a retort packed with lumps of caustic lime, kept at an orange-red heat, and passing the gas there generated through a second similar retort. He thus obtained from *crude naphtha* as highest illuminating-power 10,130 cub. ft. of gas of 20½ candles. The greatest yield of gas was 27,100 cub. ft. of 14½ candles; when the yield of gas fell as low as 6000 to 8000 cub. ft. per ton the illuminating-power did not rise above 20 candles. The gas from *light oil* in sixteen experiments ranged from 18,000 to 30,000 cub. ft. per ton; the illuminating-power from 16 to 13½ candles. The highest illuminating-power obtained with *creosote oil* was 14 candles with a make of 13,300 cub. ft.; the greatest yield of gas 29,300 cub. ft. per ton, with an illuminating-power of 8½ candles. In all these experiments with tar-oils continual stoppages took place from obstinate accumulation of naphthalene in the pipes,

<sup>1</sup> *J. Soc. Chem. Ind.*, 1886, p. 561.



which seems impossible to avoid in practice ; but, apart from that, the comparatively low yield and the very low illuminating-power of the gas seem to preclude the use of tar-oils for gas-making even at the present low prices. Crude tar, treated as above in retorts charged with lumps of lime, yielded on an average 10,700 cub. ft. of  $12\frac{1}{2}$ -candle gas ; and Wright regards tar as a gas-making material dear as a gift.

Dr Kraemer (priv. comm.) also holds that the treatment of coal-oils for the purpose of illuminating-gas is irrational. In this process but a small proportion of olefins is formed, mostly free hydrogen and hydrocarbons of small illuminating-power, as proved by trials made by the Badische Anilin- und Sodafabrik.

*Other Methods for distilling Coal-tar.*

Pfropfe (Ger. P. 28838) combines the working up of spent lye from the extraction of sugar from molasses with the distillation of coal-tar. He mixes the spent lye with ground peat and afterwards with coal-tar, and ultimately distils the whole by means of steam. A porous coke remains behind, from which alkali can be extracted by water. This process was tried on the large scale, but the resulting tar-oils were worthless, and the enormous quantity of noxious gases evolved caused the work to be stopped after a very short time. According to another patent of Pfropfe's (96763), tar is mixed with half its weight of sawdust, moulded into blocks, and distilled. The distillate is to be worked up for benzol, etc., on the one hand, and for acetene and acetic acid on the other ; the residue is said to consist of pure charcoal. All this appears very doubtful.

Markl (Ger. P. 277502) mixes tar with a very dilute aqueous alkali solution, allows to settle, and distils the separated tar. The oily fraction passing over after the water is a mobile liquid having a high calorific value, whilst the residue is an asphaltic pitch.

Melamid and Grötzinger (B. Ps. 9856 of 1912, 5484 of 1913 ; Ger. Ps. 264811, 276765, 278192 ; Fr. P. 443650) treat tar or tar-oils with phosphoric acid by heating and vigorous agitation.

The Soc. an. "Cava" at Montegnée-les-Liège, Belgium (B. P. 29897, of 1912 ; Fr. P. 452344), treats petroleum residue

("mazout") or coal-tar so as to distil off the volatile constituents and at the same time to oxidize heavy hydrocarbons and to form pitch. The tar, etc., is heated in a horizontal cylindrical retort, not above  $200^{\circ}$  to  $250^{\circ}$ , and a current of air is passed through the retort above the level of the liquid, which is kept agitated by means of blades mounted on a revolving shaft. Some of the lighter products are oxidized, so that the amount of the bituminous substances in the pitch increases, as well as the yield of pitch, without any increase of free carbon.

A similar process has been carried out by Davidson, at Dessau (quoted by Purves, *J. Soc. Chem. Ind.*, 1915, p. 331).

H. W. Robinson (B. P. 20767, 1913) treats coal-tar before or during the distillation with ozonized air or steam, in order to avoid the "creeping-back."

*Time required for working off the Tar-stills.*

In the case of tars of well-known quality the *duration of the distillation* and the *quantity of the distillates* furnish valuable indications for changing the receivers. The former must evidently vary much, according to the size and even the shape of the stills, and according to whether the distillation is carried on with or without the application of steam, of a vacuum, etc.

The distillation of raw tar takes considerably more time than that of dehydrated or even of merely centrifugalled tar, as the water contained in the tar is of very great importance for the duration of the distillation. Some gas tars containing much "free carbon," and tars of very viscid quality must be distilled with very great caution, and therefore slowly, whilst coke-oven tars containing but little carbon can be distilled very rapidly, especially in the dehydrated state. General rules for the duration of the distillation cannot, therefore, be given, and we must content ourselves with quoting a number of special cases.

In Paris the distillation of  $6\frac{1}{2}$  tons lasts 31 or 32 hours, cooling included. The first runnings and light oil run 14 hours.

At a London works a still of 2000 gall. (say 10 tons) capacity is worked off every 24 hours. Fourteen hours are reckoned for the distillation, 10 hours for cooling down, running the pitch, cooling again, and recharging.

Very small stills, of 1200 gall. (= 6 tons) capacity, are finished in 11 or 12 hours. The fire is slackened an hour

after commencing; an hour later the distillation begins, and the heavy oils come over 6 hours after that.

At a German works the horizontal 18-ton stills take 52 hours for working off and 12 hours for cooling. At another factory the stills (very large, holding 40 to 50 tons) take only from 36 to 42 hours for working off and 6 hours for cooling. At a third works 25-ton stills take 36 hours. At another German works they reckon with 15-ton stills 4 hours to the beginning of the distillation, 19½ hours for light oil, 2 hours for carbolic oil, 1 hour for anthracene oil, and 12 hours till running off the pitch. None of these factories worked with a vacuum.

At an English works known to me the first runnings from a 22-ton still take 10 hours, the light oil (up to sp. gr. 1.0) 6 hours, creosote oil (including anthracene oil) 12 or 14 hours; cooling down till the pitch is run off, 12 hours. Immediately after, the stills are recharged.

According to Watson Smith, in Lancashire 20-ton stills (steam being employed at the close) were worked off four times per week when anthracene oil was not worked for; in the opposite case, three times per week, or seven times per fortnight. 10-ton stills are worked off six times per week.

In the factories controlled by Dr Kraemer the time of working off their 15-ton stills is 10 to 11 hours, inclusive of charging and of running off the pitch, but only when working with previously dehydrated tar in a continuous way.

According to Rispler (*Chem. Zeit.*, 1910, No. 31) upright stills working charges of 32 tons of Vienna gas-tar (with about 24 per cent. free carbon) required in 1894 to 1897 two days, with interruptions at night, so that the distillation itself lasted from 28 to 32 hours. The same author, when working with 18-ton stills, reports the following data with previously dehydrated tar. The stills were heated up at 6 A.M. (the "first runnings" having been driven off during the dehydration); at 9 A.M. came the "middle oils," at 10.30 the creosote oil, at 11.45 the anthracene oil; at 1.30 the firing was stopped and the last distillate brought over by a vacuum while the fire was burning out; at 4 the pitch was run into the pitch-cooler, and at 4.30 the still was charged with fresh tar. Hence the distillation of 18 tons required only 11 hours.

*Consumption of Fuel.*

At the Paris gas-works (distilling the tar in horizontal stills without a vacuum), for  $6\frac{1}{2}$ -ton stills 14 hectolitres "coke aggloméré" was consumed.

Rispler (*loc. cit.*) states the fuel for the 32-ton stills, working non-dehydrated gas- and coke-oven tar, at 7.5 per cent. of the tar, and  $3\frac{1}{2}$ d. extra for steam; for the 18-ton stills, working dehydrated tar in a vacuum, 7.5 to 8.5 per cent. including the dehydration, and  $2\frac{1}{2}$ d. to  $3\frac{1}{2}$ d. per ton of tar for steam.

Warnes (*J. Gas Lighting*, 1910, p. 132) states that horizontal retorts require both more time and more fuel than upright retorts, viz., the former 3.5 cwt. and the latter 1.5 cwt. per ton of tar. The fuel used in England for the distillation of tar is partly coal, partly coke, and partly producer-gas. He prefers heating by producer-gas, not merely on account of the greater cleanliness and the easier attendance, but also on account of cost. In a special case the cost of heating by producer-gas was only 0.48d. per ton, against 0.84d. for heating by coal.

In Germany during recent years the heating of tar-stills by producer-gas, as well as by tar-oils, has found much attention.

Petersen-Kinberg (*Wie eine moderne Teerdestillation, etc., eingerichtet sein soll*, 1904, p. 60) makes the following statements concerning a 5-ton still, heated by coal of average quality.

*1st stage: Heating-up.*—Coal burned (without a vacuum) 60 kg.; time required, two hours. The pumping of tar into the still commences three-quarters of an hour before lighting the fire. Temperature about  $70^{\circ}$  (thermometer placed in the vapour at the overflow pipe).

*2nd stage: First Runnings and Light Oil.*—Consumption of coal, when working from  $130^{\circ}$  in a vacuum about 150 kg., without a vacuum 168 kg.; time required, five hours. The temperature rises from  $70^{\circ}$  to  $206^{\circ}$ . The latter corresponds to a specific gravity of the oil, running out of the cooler, of 1.0 at  $20^{\circ}$ . Consumption of cooling-water about 0.89 cb.m. At the end of this stage the temperature of the cooling-water ought to be about  $70^{\circ}$  (not below  $65^{\circ}$ ). The mixture of first runnings and light oil has a specific gravity of 0.96 at  $15^{\circ}$ .

*3rd stage: Carbolic Oil.*—Consumption of coal when working

with a vacuum 38 kg., without a vacuum 45 kg.; time required, one hour. The oil comes over between 206° and 240°. At 240° it has a specific gravity of 1.029 at 20°. Consumption of cooling-water about 0.27 cb.m.; temperature of it when changing for creosote oil 78° to 80°. Specific gravity of the mixed carbolic oil = 1.015 at 15°. When working for "prepared tar," the distillation is finished at 210°; or else it is driven up to 240° to obtain more carbolic acid, and the residue diluted with creosote oil.

*4th stage: Creosote Oil.*—Consumption of coal with a vacuum 30 kg., without a vacuum 33 kg.; duration, 1½ hours. Temperature rising from 240° to 264°; the latter corresponding to a specific gravity of the oil then coming over of 1.045 at 20°. Consumption of cooling-water about 0.34 cb.m.; temperature of it when changing for anthracene oil about 85°; specific gravity of the whole oil 1.035 at 15°.

*5th stage: Anthracene Oil.*—Consumption of coal with a vacuum, when working for soft pitch, 40 kg., for hard pitch 55 kg.; without a vacuum 46 resp. 65 kg. Temperature rising from 264° to 296° in the case of soft pitch, and to 315° for hard pitch. 296° corresponds to a specific gravity of the oil running out from the cooler = 1.07 at 20°; 315° to specific gravity of the oil = 1.08 at 20°. Consumption of cooling-water for soft pitch = 0.32 cb.m., for hard pitch = 0.45 cb.m. Temperature of it when stopping at soft pitch = 86°, at hard pitch = 87°. Specific gravity of the anthracene oil in both cases = 1.055 at 15°.

Altogether for a 5-ton still: consumption of coal with a vacuum, when distilling up to soft pitch, 328 kg., without a vacuum 355 kg. When distilling up to hard pitch with a vacuum 343 kg., without a vacuum 374 kg. Consumption of cooling-water up to soft pitch 1.82 cb.m., up to hard pitch 1.93 cb.m.

### *Yields.*

In the following tables the yields of the different fractions obtained in distilling coal-tar from various sources are given. But these data are not directly comparable one with another, as we have seen that the fractionating is not done in the same way in all factories.

*English Tars.*

To simplify matters, we shall at the same time quote the quantity of the final products, wherever they are stated. We shall, however, leave out some of the tables contained in the former editions of this treatise, to make room for more recent data.

*Average of my own Results with 1 ton of Tar from the Midland Counties.*

Ammoniacal liquor	.	.	3 gall.
First runnings	.	.	5.5 to 8, average 6.33 gall.
Light oil	.	.	13.5 to 15 gall.
Creosote oil	.	.	68 gall.
Pitch (hard)	.	.	11 cwt.

*Final Products from the Same.*

	Average.	Minimum.
50 per cent. benzol	3.30	3.06 gall.
Best naphtha	2.40	2.48 "
Burning naphtha	1.50	1.62 "
Creosote oil directly distilled.	68	— "
" " total	80	80 "
Pitch (hard)	11 cwt.	11 cwt.

The following statements are from *Chemistry, by Writers of Eminence*, Mackenzie, i., pp. 500 and 506.

The average produce from 1200 gall. of tar (about 6 tons) is:—

		Per cent. by weight.
Ammoniacal liquor	about 50 gall. =	about 4
First light oils	" 20 "	" 1.5
Second light oils	" 20 "	" 1.5
Creosote oils	" 250 "	" 22
Anthracene oils	" 50 "	" 4
Pitch	" 4 tons	" 67

According to Letheby, 1 ton of gas-coal, as distilled in London, gives about 9 to 10 gall. of tar; 1 ton of coal as distilled in the provinces gives about 15 gall. of tar; 1000 gall. of London tar yield:—

Ammoniacal liquor	.	.	20-28 gall., average 24 gall.
Crude naphtha (first light oils)	.	.	12-20 " " 16 "
Second light oils	.	.	4.8-14 " " 12 "
Creosote oils	.	.	275-269 " " 288 "
Pitch	.	.	3.2-4 tons " 3.5 tons

After purification these light oils yield :—

	Gallons.	
40 per cent. benzol . . .	3·44	} = 6·84 at 90 per cent.
90 " " . . .	5·31	
Solvent naphtha . . .	4·18	
Last runnings . . .	1·2	
Total dead oils . . .	301·87	

A. J. Dickinson gives as the average yield from 1000 gall. of London tar :—

	Gallons.	Per cent. by volume.
Naphtha (containing 6 per cent. benzol)	30	3
Ammoniacal water . . .	30	3
Anthracene (at 25 per cent.) . . .	10	1
Pitch . . .	650	65
Creosote, lubricating-oils, carbolic acid	280	28

The figures given by Letheby and Dickinson are somewhat different from the following, given on oath, in the course of a lawsuit, as the average yield of London tar (supplied to me by the kindness of Mr S. B. Boulton). The first column represents the results obtained at the Silvertown works of Messrs Burt, Boulton, & Haywood; the second, those obtained at the Beckton works of the Gas-Light and Coke Company (these two being among the largest tar-distillers in the world). In the first column all the oils are dehydrated and the water is included in the percentage of ammoniacal liquor :—

	Silvertown.	Beckton.
Ammoniacal liquor . . .	4·16	2·00
Crude naphtha . . .	{ 1·50 of 45% at 120°	1·66 of 30% at 120°
Light oil . . .	1·16	1·62
Creosote (containing naphthalene) .	14·16	15·70
Anthracene oil (strained or green oil)	14·00	18·83
Anthracene, 300 per cent. . .	1·80	1·90
Pitch . . .	60·00	56·29
Loss . . .	3·22	2·00
	<u>100·00</u>	<u>100·00</u>

Watson Smith obtained in 1869 from Lancashire tar, mostly made from cannel-coal, the following results:—One thousand gall. of tar of sp. gr. 1·16 = 5·3 tons, yield:—

		Per cent. by weight.
Ammoniacal liquor (4 per cent.)	25 gall.	= 2·2
First light oils	28 „	= 2·2
Second light oils	131 „	= 10·6
Creosote oils	87 „	= 7·6
Anthracene oils	191 „	= 16·9
Pitch	3½ tons	= 60·5

On further rectification these distillates yielded:—

90 per cent. benzol	about 6 gall.
Solvent naphtha	74 „
Carbolic acid	6½ „
30 per cent. anthracene	0·50 cwt.
Equal to pure anthracene	0·15 „

According to Watson Smith, the richest and best tar comes from small gas-works, because at those works the greatest possible yield from the coal is not, as at the large works, a primary consideration. There are contractors who drive about the country buying up such small lots of tar and gas-liquor, and taking them to the tar-distillers for sale.

Compare also the results obtained by Köhler, quoted p. 442.

The following table, compiled by Sir Henry Roscoe from statements collected by Watson Smith and I. Levinstein, represents the average yield of products from Lancashire tar, together with some interesting statements concerning the dyeing-power of the artificial colours derived therefrom<sup>1</sup>:—

*One ton of Lancashire Coal yields, when distilled in Gas-retorts, on an average:—*

Gas (cubic feet).	Ammoniacal liquor, 5° Tw.	Equivalent to Ammonium sulphate.	Coal (gas) tar, sp. gr. 1·16.	Coke.
10,000	20 to 25 gall.	30 lb.	12 gall. = 139·2 lb.	13 cwt.

<sup>1</sup> Lecture delivered at the Royal Institution, 16th April, 1886, p. 7.



*Twelve gallons of Gas-tar yield (average of Manchester and Salford Tar):—*

Benzene.	Toluene.	Phenol proper.	Solvent Naphtha for Indiarubber, containing the three Xylenes.	Heavy Naphtha.
Lb. 1.10 = Aniline 1.10	Lb. 0.90 = Toluidine 0.77	Lb.  Aurin 1.2	Lb. 2.44 yielding 0.12 Xylene= 0.07 Xylidine.	Lb. 2.40
= Magenta 0.623 or 1.10 lb. Aniline yield 1.23 lb. Methyl Violet.				

Naphthalene.	Cresote.	Heavy Oil.	Anthracene.	Pitch.
Lb. 6.30 = $\alpha$ Naphthylamine 5.25 = $\alpha$ or $\beta$ Naphthol 4.75 = Vermilline Scarlet, RRR 7.11, or = Naphthol Yellow * 9.50	Lb. 17.0	Lb. 14	Lb. 0.46  Alizarin 20% 2.25	Lb. 69.6

\* The naphthol yellow is a representative colour from  $\alpha$  naphthol, while the vermilline scarlet is a representative colour from the combination of  $\alpha$  naphthylamine with  $\beta$  naphthol.

*Dyeing-powers of Colours from 1 ton of Lancashire Coal.*

Lb. 0.623 Magenta dye 500 yards 27 inches wide Flannel a full shade.	or	Lb. 1.23 Methyl Violet dye 1000 yards 27 inches wide Flannel a full Violet.
Lb. 9.50 Naphthol Yellow dye 3800 yards 27 inches wide Flannel a full Yellow.	or	Lb. 7.11 Vermilline dye 2560 yards 27 inches wide Flannel a full Scarlet.
Lb. 1.2 Aurin dye 120 yards 27 inches wide Flannel a full Orange.	or	Lb. 2.25 Alizarin 20 % dye 255 yards Printer's cloth a full Turkey Red

*Dyeing-power of Colours from 1 lb. of Lancashire Coal.*

Magenta a piece of Flannel 8 in. by 27 in.	or Violet a piece of Flannel 24 in. by 27 in.	Yellow a piece of Flannel 61 in. by 27 in.	or Scarlet a piece of Flannel 41 in. by 27 in.
Orange a piece of Flannel 1-93 in. by 27 in.	Turkey Red a piece of Flannel 4 in. by 27 in.		

The following statistics have been kindly supplied to me by Mr Wilton, manager of the Beckton tar-works, as representing the production of the United Kingdom in 1885:—

	Gallons	= Tons
Ammoniacal liquor from tar alone .	3,600,000	1,200 (of sul-
Carbolic acid (crude) . . . . .	600,000	phate).
Creosote oil . . . . .	21,600,000	
Of this there was liquid creosote .	10,800,000	
"    "    creosote salts . . . . .		56,620
(= crude naphthalene)		
corresponding to pure naphthalene . . . . .		25,310
Green oil . . . . .	24,000,000	
Benzol and toluol . . . . .	1,500,000	
Solvent naphtha . . . . .	620,000	
Anthracene (pure)=6,840,000 units= . . . . .		3,420
Pitch . . . . .		396,000

Total quantity of tar distilled, 120 million gall.; say 645,000 tons.

A statement in the *Chem. Zeit.*, 1879, p. 148, puts the yield from 11,250 litres (= 10 tons) of London tar at:—

50 per cent. benzol . . . . .	12-96 litres =	1-1 per cent.
Solvent naphtha . . . . .	12-15 " =	1-0 "
Burning naphtha . . . . .	16-75 " =	1-4 "
Creosote oil . . . . .	373-5 " =	35-0 "
Anthracene cake (30 per cent.) . . . . .	11-25 " =	1-0 "
Pitch . . . . .	5870 kg. =	58-6 "

On the results obtained with English coal-tars during more

recent times, R. Warnes (*J. Gas Lighting*, 1910, p. 132) makes the following statements:—

	Yorkshire tars.		North Country tars.	Midland tars.
	A.	B.		
Water . . .	7.3 gall. per ton	1.8 gall. per ton	11.5 per cent.	4.50 gall. per ton
Crude naphtha .	14 "	10.5 "	0.9 "	4.36 "
Light oil . .	23 "	12.3 "	3.0 "	18.20 "
Middle oil . .	...	...	...	9.20 "
Creosote oil .	35.1 "	53.5 "	15.6 "	} 31.80 "
Anthracene oil .	28.1 "	6.0 "	10.4 "	
Pitch . . .	9.3 cwt.	11.5 cwt.	57.5 "	

Wyne-Roberts (*ibid.*) makes the following statements concerning various furnaces:—

	Specific gravity at 16°.	Free Carbon.	Water.	Light oils up to 170°.	Middle oil up to 270°.	Creosote oil up to 360°.	Anthracene oil.	Pitch.	Naphthalene.
		per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Tar from horizontal retorts	1.20	abt. 20	...	3.10	7.68	10.15	11.64	62.00	...
	1.25	...	...	1.10	13.10	13.20	...	72.60	...
	1.22	...	6.0	1.40	10.50	16.14	...	81.80	...
	1.22	28.70	...	1.10	13.10	13.20	...	72.10	9.00
Tar from vertical retorts	1.10	2 to 4	...	5.85	12.32	11.95	15.95	49.75	...
	1.12	0.40	...	1.70	21.90	21.60	...	54.80	3.60
	1.119	4.20	...	3.70	20.20	23.10	...	52.60	4.80
	1.13	0.60	...	2.30	16.50	20.80	...	60.00	3.60
Tar from slanting retorts	1.095	2.60	2.20	4.40	28.20	19.20	...	47.50	...
Tar from chamber ovens	1.18	11.10	10.10	0.40	10.20	30.10	...	53.90	4.70
Tar from coalite	1.07	...	...	10.80	20.00	30.00	...	39.20	...

#### German Tars.

*Tar from the Berlin Gas-works* ("Chem. Ind.," 1879, p. 282).

	Per cent.	Per cent.
Benzol (including toluene, etc.)	0.80	
Other colourless oils (higher homologues)	0.60	
Crystallized carbolic acid	0.20	
Cresol for disinfecting purposes	0.30	
Naphthalene	3.70	
		5.60
Creosote oil		24.00
Anthracene (pure)		0.20
Pitch		55.00
Water and loss		15.20
		<u>100.00</u>

According to Häussermann (*Industrie der Theerfarbstoffe*, 1881, p. 13), 100 parts of tar from German coals yield—

5 to 8	per cent.	light oil,
25 „ 30	„	creosote oil,
8 „ 10	„	anthracene oil,
50 „ 55	„	pitch.

The final products are—

0.6	per cent.	benzene,
0.4	„	toluene,
0.5	„	higher homologues,
8 to 12	„	pure naphthalene,
5 „ 6	„	phenol,
0.25 „ 0.3	„	anthracene (pure).

According to G. Schultz (*Chemie des Steinkohlentheers*, 2nd ed., vol. i., p. 67) there were obtained, in a Rhenish tar-works, from 100 parts of tar:—

	Per cent.
Purified benzol (for aniline and as a detergent)	1.00
Pure anthracene . . . . .	0.33
Pure naphthalene . . . . .	2.00
Creosote oil . . . . .	30.00
Pitch . . . . .	60.00
Ammoniacal liquor . . . . .	2 to 10.00

Kraemer and Spilker<sup>1</sup> make the following statements, founded on the results of a number of the largest German tar-works. Heavy tars, with 25 per cent. and upwards of carbon and sp. gr. over 1.21, yield from 32 to 35 per cent. oily distillates. Normal tars, of sp. gr. 1.16 to 1.20, yield 38 to 40 per cent. oils, lighter coke-tars 42 per cent. and more. At four German factories, working with different raw material, but otherwise exactly under the same conditions and with the same apparatus, the following results were obtained:—

No. I. Tar from Silesian gas-coal.

No. II. Tar from gas-works, where much Saxon coal and paraffinoid additions were used.

No. III. Tar from the coast, where mostly English coal is used.

No. IV. Tar from Saar coals, with addition of paraffinoid coal.

<sup>1</sup> Muspratt-Stohmann's *Techn. Chemie*, 4th ed. (1905), viii., p. 14.

*Results of Distillation per cent.*

No.	Water.	Pitch.	Total oils.	Light oil, 0·910-0·960.	Middle oil, 1·01.	Creosote oil, 1·04.	Anthracene oil, 1·10
I.	3·0	55·1	41·3	2·1	12·0	9·2	18·0
II.	4·9	52·2	41·8	2·5	12·9	11·2	15·2
III.	3·1	59·9	37·0	3·3	9·4	7·0	17·0
IV.	4·1	59·4	35·0	3·8	10·8	8·6	12·1

The yield from normal tars may be taken as follows:—

	Sp gr.	
Light oil . . .	0·910 to 0·950	2 to 3 per cent.
Middle oil . . .	1·01	10 „ 12 „
Creosote oil . . .	1·04	8 „ 10 „
Anthracene oil . . .	1·10	16 „ 18 „

*Coke-tars* (according to those authors) do not materially differ from gas-tars. On the whole they yield less benzol and phenols, but rather more anthracene. *Oil-gas tars*, however, possess quite a different character, corresponding to the paraffinoid nature of the raw material. They yield no phenols and very little pyridines, and the oils contain much less aromatic compounds. Oil-gas benzol always contains much olefins: the middle oils contain but little naphthalene, and the heavy oils hardly any anthracene, which is, moreover, contaminated with methylanthracene, etc. *Blast-furnace tars* occupy an intermediate position between coal-tars and oil-gas tars.

According to Heusler (*Chem. Technologie*, 1905, p. 188) a German tar-works in the year 1893, using both gas-tar and coke-oven tar, had the following yields of pure products:—

	Per cent. of the tar.
Benzol and toluol . . . . .	0·22
Xylol and solvent naphtha . . . . .	0·62
Phenol . . . . .	0·40
Cresols . . . . .	1·13
Naphthalene . . . . .	6·40
Pure anthracene . . . . .	0·44

According to the same author, Upper Silesian coke-oven tar on the average of several years yielded 20 per cent. anthracene oil, from which 0·5 to 0·7 per cent. pure anthracene (calculated on 100 raw tar) was obtained. Various descriptions of Upper Silesian tar yielded 0·5 to 2·2 per cent. benzols. He estimates the true percentage of cresol at 2·0 per cent., that of naphthalene at 9 to 10 per cent.

According to a prospectus issued in 1896 by the Badische Anilin- und Sodafabrik, 1000 kg. coal yield 50 kg. tar, and these again yield 0.4 kg. benzols (=0.3 kg. magenta or 0.5 kg. aniline blue); 0.3 anthracene (=0.3 alizarine or 0.3 alizarine blue); 1.0 naphthalene (=0.35 kg. indigo).

Rispler (*loc. cit.*) quotes the average results obtained by the Imperial Continental Gas Association in Vienna with gas-tar, containing about 24 per cent. free carbon, distilled in 32-ton stills without a vacuum during the years 1894 to 1896:—

	Per cent.
Ammoniacal liquor . . . . .	4.27
Light oil . . . . .	4.06
Middle oil . . . . .	10.38
Creosote oil . . . . .	6.11
Anthracene oil . . . . .	13.71
Pitch . . . . .	60.49
Loss . . . . .	0.98
	<u>100.00</u>

The average yield from coke-oven tars in the Ruhr district during a number of years, according to Spilker (I.) and Rispler (II.), are as follows:—

	Per cent. I.	Per cent. II.
Ammoniacal liquor . . . . .	2.69	3.86
Light oil . . . . .	1.38	1.24
Middle oil . . . . .	3.46	12.02
Creosote oil . . . . .	9.93	8.50
Anthracene oil . . . . .	24.76	18.68
Pitch . . . . .	56.44	54.56
Loss . . . . .	1.34	1.14
	<u>100.00</u>	<u>100.00</u>

Belgian tar, distilled after dehydration in 18-ton stills with a vacuum, according to Rispler, yielded the following average results:—

	Per cent.
Ammoniacal liquor . . . . .	4.14
Light oil . . . . .	1.08
Middle oil . . . . .	7.38
Creosote oil . . . . .	7.90
Anthracene oil . . . . .	20.26
Pitch . . . . .	58.24
Loss . . . . .	1.00
	<u>100.00</u>

The *costs* of distilling a ton of this tar were as follows :—

	Marks.
Wages . . . . .	0.39
Coal (2.5 per cent.) . . . . .	1.13
Steam . . . . .	0.24
Sundry materials . . . . .	0.02
Repairs . . . . .	0.22
Amortisation . . . . .	0.65
	<u>2.65</u>

The price of coal was 15.0 mark per ton, the wages per ton 5.0 mark for the foreman, and 4.5 mark for the attendant to the stills.

The *cost of wages* and the amount of *amortisation* is greater in the case of gas-tar than in that of coke-oven tar, owing to a longer time for distilling, etc., in the following proportion, according to Rispler :—

	For gas-tar.	For coke-oven tar
Wages . . . . .	0.81 marks	0.51 marks
Coal (7½ per cent.) . . . . .	1.13 "	1.13 "
Steam . . . . .	0.35 "	0.35 "
Sundry materials . . . . .	0.12 "	0.12 "
Repairs . . . . .	0.31 "	0.31 "
Amortisation . . . . .	1.35 "	0.84 "
	<u>4.07</u>	<u>3.26</u>

The cost of distilling, of course, also depends on the quantity worked up and on the way of distilling, as pointed out by Rispler.

Statements of the yields of products from distilling coke-oven tars have been made on pp. 147 *et seq.*; from water-gas tar on pp. 181 *et seq.*

On the *working-capacity of a tar-distilling plant* Rispler (*loc. cit.*) makes the following statements. This capacity depends both on the nature of the tar and of the style of working. *Gas-tar*, with its high percentage of water, considerably prolongs the time of distillation, so that 32-ton stills can only be worked off twice per week. The high percentage of free carbon in gas-tar leads to a strong deposition of coke, necessitating frequent cleanings of the still, at least once after five evaporations. Altogether, a 32-ton still gets in twelve months, that is in 300 working-days, through 2400 tons of

gas-tar. By the application of a *vacuum*, the separation of coke is diminished, and better results are obtained. The distillation of coke-oven tar in a vacuum admits of working off 30 charges before the still requires cleaning out, so that a 32-ton still gets through 3840 tons of tar *per annum*. When working with dehydrated tar in a vacuum, an 18-ton still allows of making 30 operations before having to be stopped for cleaning. In 300 working-days 270 charges of 18 tons each can be made, that is 4860 tons of dehydrated tar, corresponding to 5050 tons raw tar.

*Testing of Tar on a small scale or in the Laboratory.*

If a sample of tar has to be tested for its yield on a smaller scale, its distillation must be carried on in exactly the same way as on the large scale. The result will be all the more reliable the larger the scale of the testing operation. When distilling, say, 10 gall., the results will be only approximative, especially for benzol and naphtha. It is better to employ small stills holding 80 to 100 gall.; but it is even preferable to distil 200 to 250 gall. from a light oil still (Chapter X.). The products are separately weighed and measured; and light oil and naphtha are tested for their yield of benzol and naphtha according to the rules given at the close of Chapter XI.

Where the testing of tar must be performed with ordinary laboratory appliances, the following hints by Watson Smith<sup>1</sup> will be found extremely valuable, and are therefore quoted *in extenso* :—

“It is well known to those who have attempted the distillation of samples of coal-tar (wood-tar is just as difficult to manage) that, owing to the invariable presence of water, often in considerable amount, there is extreme difficulty in the earlier stage of the process to prevent boiling or frothing over of the contents of the retort. Sometimes disproportionately large iron retorts are used for such trials of small quantities of tar, in order to leave as much room as possible for frothing up. By the method about to be described, we have used, in the laboratory of the Owens College, only large glass retorts, holding

<sup>1</sup> *J. Soc. Chem. Ind.*, 1883, p. 496.



about  $2\frac{1}{2}$  litres when filled to within  $\frac{1}{4}$  of an inch of the beak of the retort, and have found no difficulty in fractionating the tar in such apparatus when the proper precautions were observed. The following are the salient points in the method I have devised:—

“The tar is first freed from water as much as possible, by placing the containing vessel (*e.g.*, a large glass beaker) in hot water, and allowing to stand for about a day and night, the beaker being well covered with a glass plate. The reduction thus effected of the density and tenacity of the tar allows of the separation of water with greater facility. If the tar be heavier than water it settles down, and the water rises, forming a layer, which, after allowing to cool, may be decanted off. Frequently a great deal of water may be got rid of by inclining the vessel alternately in different directions, when, if the tar be a heavy one, the water collects and flows to the point of inclination more rapidly, and so the portion accumulated may be decanted off before the tar reaches that point. In the case of a tar or tar-oil lighter than water, a subnatant layer of water forms by the warming and settling process; and in this case a tolerably wide siphon or run-over might be used, or, from a beaker, the tar-oil might be merely decanted.” For the *specific gravity determination*, “a measured quantity of tar (say 1 litre), settled or partially dehydrated as above, is run into a previously tared vessel, and, after cooling to  $15^{\circ}$  C., the latter, with its contents, is weighed. These data are sufficient for the specific gravity. The ordinary specific-gravity bottle would be a clumsy contrivance in this case. For the *distillation* about  $2\frac{1}{2}$  litres of tar are taken and poured into a large glass retort arranged on a stand in the usual way. The stand is placed in a large iron tray with high sides (about 6 to 7 in.), the bottom of which is covered with sand to the depth of  $\frac{1}{2}$  an inch or so. This arrangement is to afford protection to the operator, in case of accident. A glass tube, besides the thermometer, is inserted through the cork acting as a stopper. This tube is drawn out to a small aperture, and is caused to dip about half-way to the bottom of the retort from the surface of the tar. A slow current of air is passed through the tube and forced through the tar, and the temperature of the tar is carefully and not too quickly raised to from  $60^{\circ}$  to  $70^{\circ}$  C. This temperature is maintained, if necessary, for

a day or two, until all ammonia-water is expelled. If the tar be a heavy one, a layer of ammonia-water may form on its surface after heating to  $60^{\circ}$  to  $70^{\circ}$  for some time. If the layer be of considerable thickness, it will be advisable to remove the stopper and decant it off. Frequently a slow distillation for about a day or more may thus be spared by an operation lasting a few minutes only. If the tar contains much spirit or benzol, the receiver, which should be one with a second opening, admitting a cork, is connected with a wash-bottle containing some heavy oil, to retain naphtha vapours else carried off by the air-current. The naphtha is afterwards recovered by blowing wet steam through the oil, the vessel being connected with a condenser. The volume of the naphtha is then measured. When all water is removed from the tar, the distillation will proceed quite smoothly."

I may also be allowed to quote my own directions for testing tar in the laboratory, as given in the *J. Soc. Chem. Ind.*, 1887, p. 581 :—

"Such an investigation cannot be expected to yield useful results, unless somewhat large quantities are taken in hand. But in a scientific laboratory it is difficult to employ more than a few kilograms for each distillation. The results thus obtained will never exactly coincide with those obtained in manufacturing practice, but experience proves that they give a very good idea of the general quality of the tar. It would be most convenient to employ for such quantities distilling vessels made of metal, and I would, indeed, strongly recommend this for factory laboratories, all the more as it is thus easy to work upon very much larger quantities. But in scientific laboratories, where, for more reasons than one, it is out of the question to distil a hundredweight of tar or some such quantity, it will be always preferred to accurately observe the progress of the operation, and this it is only possible to do in glass retorts. Especially the dehydration of the tar, such as will be described further on, can be hardly carried out in any other way, whilst it is comparatively easily done in glass retorts. Watson Smith has also used such for his investigations.

"My retorts were tubulated, holding about 5 litres, and were heated in a kind of sand-air bath—that is, in a suitably-shaped thin wrought-iron dish, the bottom of which was covered

by a layer of sand 1 cm. thick. About half of the retort was within the dish, and the whole of it, down to the sand, and including the upper part of the neck, was wrapped round with wire gauze. The heating was done by a Fletcher's gas-stove, placed in a large flat pan, partially filled with sand. Hence, in case of an accident, the tar would have first run into the upper pan, forming the sand-air bath, and anything boiling over from this would have been caught in the lower pan.

"The tubulure of the retort was fitted with a twice-perforated cork, holding a thermometer and a tube, drawn out into a capillary at the lower end, with the object of passing a minute current of air-bubbles through the liquid, in order to prevent bumping. This precaution, first introduced by Dittmar, and also employed by Watson Smith, was found to be very useful indeed; but it seems possible that the air-current might carry away a minute quantity of benzene.

"The retort was, during the first part of the operation, connected with a Liebig's condenser, so long as the distillate remained entirely liquid. When it began to partly solidify—that is, between  $170^{\circ}$  and  $180^{\circ}$ —the cooler was removed; and since now the last portions of water had been volatilized, and no more bumping was to be apprehended, the current of air was discontinued. The last of the water escaped between  $140^{\circ}$  and  $170^{\circ}$  with explosive violence.

"The distillation of  $2\frac{1}{2}$  or 3 litres of tar took about eight hours.<sup>1</sup> It is decidedly advisable to carry it right through without any interruption, both because the heating-up, after the contents of the retort have been semi-solid or solid on cooling, is always an awkward operation, and because during the cooling-down and the heating-up a considerable quantity of substance passes over far below the proper boiling-points.

"The distillates were collected in tared, narrow, graduated cylinders, and after cooling down they were measured and weighed. The fractions were made in the way to be stated below. But although, as a matter of course, every precaution

<sup>1</sup> According to Kraemer (priv. comm.) this period can be considerably shortened by first filling the retort only about a quarter, and then gradually running in the other portion; this prevents any frothing-over.

was taken to keep the temperature as constant as possible, still, without any recognizable reason, the thermometer showed considerable oscillations, and sometimes went down  $20^{\circ}$  without any diminution in the rate of distillation.

"It cannot be said that such assays are exact analytical operations. The fractions will differ to some extent, as the distillation proceeds more or less slowly. Each time, when substances are poured from one vessel into another, small losses are unavoidable, although in the case of the higher-boiling substances the vessels were rinsed with ether, which was subsequently evaporated. In washing and drying, in the case of the first distillates also by evaporation, small losses will occur, which become all the more important when the absolute quantity of substance is only slight.

"If the tar has not been previously dehydrated, the work must begin with that operation, which is of great importance. It is not feasible to go as far as  $100^{\circ}$ , because then the tar would lose many valuable portions, especially as the operation takes so much time. Hence, the dehydration was performed in the retort itself, turning its neck upwards and connecting it with a cooler, inclined downwards, in order to collect any benzene escaping along with the water. The heating was continued in this manner to  $60^{\circ}$  to  $70^{\circ}$  for a full fortnight; every morning, before recommencing, the water collected in the meantime on the surface was removed by a pipette. For all that some water remained behind, evidently in chemical combination with phenol, pyridine, etc., and this could only be removed by distillation.

"The fractions were made as follows:—

1. Light oil, up to  $170^{\circ}$ .
2. Middle oil, up to  $230^{\circ}$  (carbolic oil).
3. Creosote oil, up to  $270^{\circ}$ .
4. Anthracene oil, up to the close of the distillation, which was continued as long as anything would come over; this explains why the pitch was extraordinarily hard.

"The above fractions were treated in the following manner:—The *Light Oil* was first agitated with caustic soda solution of sp. gr. 1.1, and the contraction of volume was calculated as 'phenols.' The oil was then washed with water, with con-

centrated sulphuric acid, and again with water, and the total contraction was calculated as 'loss by washing.' The residual oil was distilled, and the fractions coming over up to  $100^{\circ}$  and  $140^{\circ}$  were separately collected. The distillate up to  $140^{\circ}$  was considered as 'crude aniline-benzol,' and its degree of purity was examined by nitrification with the ordinary mixture of acids. The portion remaining behind at  $140^{\circ}$  was calculated as 'heavy naphtha': it must, of course, leave a good deal of residue on rectification, and this residue will practically go to the creosote oil; but, on the other hand, some heavy naphtha will come back from the 'middle oil,' and on the small scale it was impossible to say how far this would compensate for the residue left on rectifying. The small quantity of liquid also made it impossible to separate the 'aniline-benzol' into benzene, toluene, and xylenes.

"From the *Middle Oil* and the *Creosote Oil* a quantity of naphthalene crystallized on cooling. This was filtered through calico, strongly pressed, and calculated as 'crude naphthalene.' The liquid portion of the oil (making allowance for the mechanical loss in pressing) was treated with caustic soda solution, and the contraction of volume again set down as 'phenols.'

"The *Anthracene Oil*, after cooling, was filtered through calico, the crude anthracene was pressed cold, then spread out upon porous earthenware slabs, heated in an air-bath to  $30^{\circ}$  to  $40^{\circ}$ , pressed while warm, and weighed. It was now analysed by the 'Höchst' test; but since in the trade anthracene is usually sold as 30 or 40 per cent, three times the weight of pure anthracene was deducted from the weight of crude anthracene oil, to get at the figure for liquid anthracene oil.

"The *pitch* was tested for its softening point by heating a piece of the size of a pea on a wire in an air-bath beside a thermometer until, by pressing with the fingers, it proved to be distinctly plastic. The water-bath did not suffice for this purpose. It was further tested for 'carbon'—one of the most tedious parts of the work. For this purpose it was extracted alternately with boiling benzene and carbon disulphide; but it took many days' toil until the solvents did not show any but a faint colour, and left no more residue when evaporated on a watch-glass. This operation must be carried out

with the greatest caution, since otherwise fine particles of carbon will pass through the filter; for this reason Soxhlet's extracting apparatus, otherwise so convenient, could not be employed."

Rispler<sup>1</sup> describes an apparatus by means of which 5 or 6 kg. of tar may be freed from water and light oil within an hour. It is an iron cylinder, holding the required quantity, with an arched top and two necks. One of these, in the centre, is closed by a glass T-piece, in which a thermometer is placed on the top, while the lateral branch, which is slightly inclined downwards, is connected with a Liebig's cooler and receiver. The second neck of the still top is fitted with a tap, and above this a funnel, holding 1½ kg. tar and heatable by steam or hot water. The still itself is heated by a large circular burner. Weigh off 5 to 6 kg. tar; pour 1½ kg. into the funnel, which in the case of viscous tars must be heated; run about half of this into the still and heat this gradually. When the thermometer indicates 110° to 120°, run more tar into the still quite slowly, and allow the temperature to rise gradually to 130°, at which it is kept until all the tar has run in. The regulation of the distillation is facilitated by the play of the vapours in the glass T-piece. After all the tar has run in and all the water and light oil are distilled off, the tap is closed and the distillation finished in the usual manner. If only the water is to be estimated, the still is fitted with a lateral tap a little above the bottom, through which the dehydrated tar is run off. Now the next sample is gradually run in. In this manner 5 or 6 estimations of water can be made in one day. This apparatus is sold by the firm Vereinigte Fabriken für Laboratoriumsbedarf, Berlin, N., which also supplies a similar apparatus, constructed by R. Kuhn and described in *Z. für chem. Apparatenkunde*, Oct. 1905.

Other ways of testing coal-tar are described by J. Becker (*J. Gasbeleucht.*, 1902, p. 764); Senger (*ibid.*, 1902, p. 841); Kraemer and Spilker (*Chem. Ind.*, 1887, p. 337); Church (*J. Ind. Eng. Chem.*, 1911, p. 227); H. Beck (*Chem. Zeit.*, 1909); Jayne (*J. Amer. Chem. Soc.*, xxv., p. 814); Dean and Downs (*J. Ind. Eng. Chem.*, 1910, p. 195); Brown and Shadinger (*ibid.*, 1911, p. 616).

<sup>1</sup> *Chem. Zeit.*, 1905, p. 488.

*Taking Samples for testing Coal-tar.*

It is hardly necessary to mention that in the first instance the taking of a sample, really representing the average quality of the tar, must be carried out in such a way that disputes between the seller and the buyer cannot arise on that point. Senger (*J. Gasbeleucht.*, 1902, p. 841) states that in the largest Westphalian tar-works (and according to Becker, in Post's *Chem. techn. Analyse*, 3rd edition, vol. i., p. 104, also at the gas-works) the sampling of the tar is carried out by means of a tube of 2 in. diameter, open at both ends, and closed at the bottom by a cork, to which is attached a wire, passing through the tube and coming out at the top, by means of which the bottom can be opened or shut at will. This tube, after pushing down the bottom cork, is immersed in the tar, preferably in several places, and is pulled out by means of the wire, whereby the bottom cork is at the same time pulled into the tube and closes it up. The tube is cleaned on the outside and its contents are emptied into a collecting-vessel, in which the various samples are thoroughly mixed by stirring or shaking.

Jayne (*J. Amer. Chem. Soc.*, xxv., p. 814) states that the sampling of tar, arriving in cistern-wagons or tank-boats, is best performed by means of a small tap in the discharge- or pump-pipe, through which during the pumping of the tar or the emptying of the cistern, or during the filling of the transporting vessels from the tar basin, a thin stream of tar is continuously run into a vessel, the contents of which are thoroughly mixed and at once emptied into wide-necked glass bottles, before tar and water separate. This sample is specially utilised for estimating the water contained in the tar.

*Special Tests.*

*The specific gravity* of tar cannot be estimated by means of an ordinary specific-gravity bottle, which is too difficult to fill exactly and to clean in this case. I have (*Z. angew. Chem.*, 1894, p. 450) described a "weighing-bottle" of the shape shown in Fig. 130 closed by a glass stopper provided with a rill,  $\alpha$ , 2 mm. wide. The operation is performed, as when estimating the specific gravity of solids, by filling the glass only partially with tar and then completely with water. First the glass is weighed

empty (*a*), and again after filling it with water of 15° C. (*b*). It is then dried, tar is poured in up to about two-thirds of its height, and the glass, without its stopper, is placed for about an hour in hot water, till all air-bubbles disappear. After cooling, the weight of the glass plus the tar is determined (*c*). Now water is poured in, the stopper is inserted, the water issuing from the rill is removed, the whole is allowed to stand

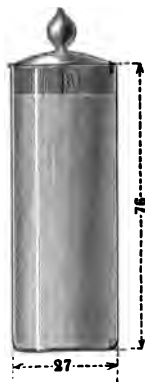


FIG. 130.

in a vessel filled with water of known temperature, and the weight is again taken (*d*). The specific gravity (*s*) sought is :

$$s = \frac{c - a}{b + c - (a + d)}$$

Church (*loc. cit.*) distils 300 to 400 g. of tar in small copper stills up to a vapour temperature of 170°, separates the mixture of water and oil passing over in a separating-funnel, and puts the oil back into the mass remaining in the still, after cooling down. He estimates the specific gravity of that mixture according to the prescriptions given by me, as just stated. For rough determinations (in the case of raw tar) he uses a hydrometer at any temperature and reduces the specific gravity thus found to the normal temperature of 15°·5, by adding to the figure found for each degree over 15°·5 : 0·000685, and deducting for each degree below 15°·5 : 0·000038.

The *coefficient of expansion* of various tars (from water-gas, gas-retorts, coke-ovens) has been fixed by J. M. Weiss (*J.*



*Franklin Inst.*, 1911, pp. 277 *et seq.*), who found only slight differences among these tars in that respect; it is practically = 0.0005. If  $V$  is the volume observed,  $t$  the temperatures in degrees Centigrade, and  $C$  the coefficient of expansion as just stated, the volume at the normal temperature of 15° C. is  $= V - V(t - 15^\circ) \times C$ . The same author (*J. Ind. Eng. Chem.*, 1915, p. 21) describes the examination of tars, tar-oils, and pitches according to well-known methods.

In most cases the specific gravity of tar, after dehydration, is a sufficient guide as to its quality. According to Köhler (*Z. angew. Chem.*, 1888, p. 677), it depends mainly upon the percentage of free carbon, as shown in the following table:—

Origin of tar.	Specific gravity.	Free carbon per cent.
Heidelberg . . . .	1.220	23.75
Darmstadt . . . .	1.215	20.93
Baden-Baden . . . .	1.195	19.92
Bockenheim . . . .	1.190	18.24
Frankfort . . . .	1.180	15.70
Bamberg . . . .	1.175	15.15
Neustadt . . . .	1.172	15.07
Cannstadt . . . .	1.164	14.05
Rottweil . . . .	1.161	14.00
Karlsruhe . . . .	1.155	13.50
Ulm . . . .	1.150	12.44
Heilbronn . . . .	1.150	12.42
Oos . . . .	1.145	5.00

*The estimation of water* in the tar has to be performed much more frequently than other tests of it, and it has been referred to in several of the foregoing descriptions of work. Payne<sup>1</sup> employs for this purpose a small copper still of cylindrical form, holding 1 litre. The upper end is surrounded by a heavy turned flange, the lid is of brass and clamped to the still by a single clamp passing over the top, a paper gasket being placed between the two metal surfaces. The condenser consists of an open trough, through which passes a slanting glass tube 27 in. long (a Liebig's condenser). Great care must be exerted in taking the sample, preferably by means of a small cock through which a small stream is allowed to flow during the pumping of the tar into or out of the boat, car, etc. The quantity thus

<sup>1</sup> *J. Amer. Chem. Soc.*, 1903, xxv., p. 814.

obtained must be violently stirred and at once fitted into wide-mouthed quart bottles or cans, before any separation can take place. Five hundred c.c. of this sample are put in the still, the lid is securely clamped and the Liebig's tube and thermometer fixed in their places. The heat must be applied very carefully, to avoid bumping and foaming over, preferably by a ring burner, which is at first placed so that the top of the still is heated; it is gradually lowered, and, in the end, an additional burner may be placed under the bottom. To be certain that all water is expelled, the thermometer in the vapour should reach 200° C. Oil and water are collected; they separate at once and the cubic centimetres of water are read off. If desired, the distillation can then be carried on until the end. Some tars are very difficult to free from water, the contents of the still boiling over in spite of all precautions. This may be avoided by adding to the tar a hydrocarbon boiling slightly higher than water, *e.g.* toluene. This thins the tar and carries over the water completely and very rapidly.

The just-named process (addition of 40 to 45 per cent. benzol to tar containing much water, in order to prevent frothing over) had been previously practised by Maywald,<sup>1</sup> and also forms the subject of a previous patent for treating petroleum.

The methods for estimating the water in tar published by Becker<sup>2</sup> and Senger<sup>3</sup> are quite similar to that of Payne.

The apparatus of Rispler (*supra*, p. 519) can also be of service for this purpose, and seems to be mostly employed for estimations of water in tar.


*The estimation of free carbon* (cf. *supra*, p. 308) in tar is decidedly important, and allows of drawing conclusions as to the best way of working it up (*vide infra*). Kraemer extracts the tar with forty times its weight of xylene. Köhler considers it more expeditious to heat 10 g. tar with a mixture of 25 g. glacial acetic acid and 25 g. toluene, pouring the liquid on to two filters of equal weight, placed one within the other, and washing with boiling benzene until this runs off colourless. After drying, the outer filter is used as tare in weighing the inner filter, containing the carbon.

<sup>1</sup> Ahrens, *Chem. techn. Analyse*, p. 211.

<sup>2</sup> *J. Gasbeleucht.*, 1902, p. 764; *Chem. Centr.*, 1902, ii. 1279.

<sup>3</sup> *Ibid.*, 1902, p. 841; *ibid.*, p. 1435.

Church (*loc. cit.*) estimates the free carbon in tar as follows. From 5 to 10 g. of tar, dehydrated up to 170°, are passed through a sieve of 30 meshes per superficial inch, and heated on a water-bath with chemically pure toluene, and then brought quantitatively on to a double cylindrical filter, which is prepared by folding the paper round a cylindrical rod of 1.5 c.c. diameter, drying at 110° and weighing. The mass on the filter is washed three or four times with pure benzene, and the filter is now placed in the vapour space of an extracting apparatus with reflux-cooler, the distilling-flask having been filled with pure benzol. The distillation in this reflux-apparatus is continued for several hours, in any case up to the point that the benzene runs colourless through the filter, whereupon the latter is dried and weighed.

Kraemer and Spilker (Muspratt's *Chemie*, 4th edition, viii., p. 3) recommend the following methods as the simplest for factory use. Mix 1 g. tar with 5 g. aniline and pour into a cup of porous porcelain of this shape:  which absorbs the liquid portion, leaving the carbon as a leaf-like mass which can be detached by means of a wooden spatula, put into a tared watch-glass and weighed after keeping in the water-bath for a few hours. The results show 2 or 3 per cent. less carbon than is obtained by Kraemer's xylene method, but are quite useful for comparative purposes.

Hodurek (*Oest. Chem. Zeit.*, 1904, p. 365) has found that the various solvents, especially benzene, glacial acetic acid, and ether, have a precipitating effect on bituminous substances, especially those contained in coal-tar pitch. If the latter is dissolved in the least possible quantity of benzol, the filtered solution on addition of an excess of benzol yields brown or reddish brown substances—just those which give to carbolineum (*cf. infra*) its characteristic colour. He therefore proceeds as follows for the estimation of free carbon in tar (and pitch). He mixes 5 g. tar with 200 c.c. 90 per cent. benzol, heats for five minutes to boiling, filters on to a dry, weighed paper filter, washes with 100 c.c. boiling benzol, dries at 100° C., and weighs. Thus he finds carbon *plus* bitumen. In a second portion of the tar the suspended carbon is removed by careful filtration through paper, and 5 g. of the filtrate are treated as above; the difference of both estimations yields the per-

centage of free carbon. [This method is troublesome and lengthy, without giving any better results than the generally used method of Kraemer and Spilker.]

An expeditious process for estimating the free carbon in tar, founded on the well-known connection between the specific gravity of tar and its contents of free carbon, which has proved to be reliable by a large number of tests, is described by Arthur R. Warnes in *J. Gas Lighting, etc.*, 1910, p. 132. He works with a Twaddle hydrometer, employing the formula :

$$\text{Free carbon} = 0.8n - 10,$$

$n$  signifying the degrees Tw. The following observations with Yorkshire and Midland tars (extraction by means of crude naphtha up to complete exhaustion) prove the reliability of the method.

Number of test.	Degrees (Twaddle.)	Carbon.	
		Determined by extraction.	Calculated by the formula.
		per cent.	per cent.
1	47	27.87	27.60
2	39	21.50	21.20
3	41	22.80	22.80
4	43	24.70	24.40
5	32	14.85	15.60
6	42	23.76	23.60
7	45.6	26.79	26.48

Hooper (*ibid.*, 1911, cxiii, p. 100) recommends the same method for estimating the free carbon in dehydrated tar. He employs, however, the following formula for calculating the percentage of free carbon from the degrees Tw. found :

$$\text{Percentage of free carbon} = 1.64n - 10,$$

in which  $n$  signifies the degrees Tw. The difference between his and Warnes' formula may be caused by the fact that Warnes employed as the basis of his formula the residue remaining after extracting the tar with crude naphtha and then washing after extracting the tar with crude naphtha and then washing with benzene, whilst Hooper effected a much more complete successive extraction in a Soxhlet apparatus first with benzol, then with pyridine, and ultimately with methyl alcohol.

The more free carbon, the more viscous the tar, and the more easily will it froth over during the distillation. Tars containing less free carbon, that is, of less specific gravity, are richer in benzene and other light hydrocarbons than those containing more free carbon. But this holds good only to a certain limit, say, 15 or 17 per cent. free carbon. Above this tars of equal percentage of free carbon may furnish either more anthracene or more benzene, etc., according to their origin. But if they contain considerably more carbon than 17 per cent., they are sure to yield less valuable products of all kinds and more pitch.

If  $K$  is the percentage of free carbon in the pitch and  $k$  the percentage of free carbon in the tar, the yield of pitch is  $\frac{100k}{K}$ . Moderately hard pitch contains about 28 per cent. free C.; for normal tar with 16 per cent. we thus find a yield :

$$\frac{100 \times 16}{28} = 57 \text{ per cent.},$$

which is in sufficient agreement with experience in the case of ordinary gas-tars, but not in the case of coke-oven tars, and tars containing but little free carbon, like those from vertical ovens and chamber-ovens.

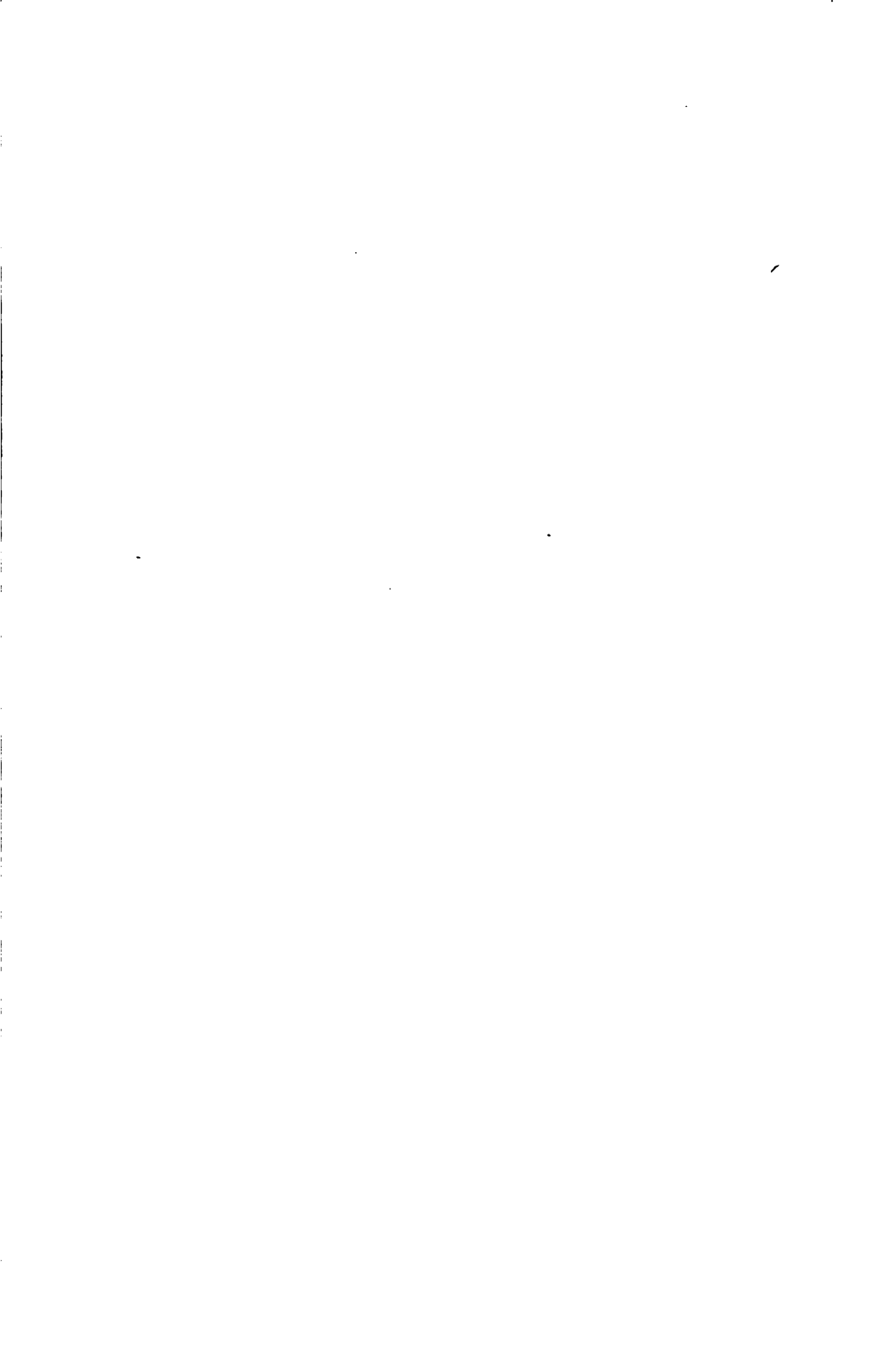
The estimation of the *coking-residue*, of *volatile substances*, and of *ashes* are carried by the ordinary well-known methods. Church (*loc. cit.*) proceeds as follows: 1 g. tar is heated in a platinum crucible with tightly closing cover on a platinum triangle, placed from 6 to 8 c.c. above the top of a Bunsen burner in a room not subject to draughts, until the upper side of the cover is free from soot, but the lower side still covered with soot. The residue is to be considered as the "coking-residue"; the loss of weight, deducting the previously determined percentage of water, indicates the "volatile substance." For estimating the percentage of ashes, 10 g. of the tar are burned in an open platinum or porcelain crucible, and ignited up to the weight remaining constant.

The estimation of the *viscosity* of the tar is important for its use of fuel. It is carried out by means of Engler's viscometer at various temperatures (according to Church at 60°) and expressed in Engler degrees. It varies within wide limits; Allner (*loc. cit.*)

found from  $16^{\circ}$  to  $138^{\circ}$  in the case of horizontal oven-tars, and from  $1.8^{\circ}$  to  $4.5^{\circ}$  (at  $50^{\circ}$ ) in the case of vertical oven-tars. (Engler's viscometer is described in Lunge-Keane's *Technical Methods of Chemical Analysis*, 1914, vol. iii., p. 68). Cf. also the examination of the viscosity of varnishes in Chapter VI.

END OF PART I.

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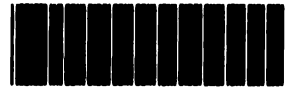
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